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METHODS OF AIR ANALYSIS.

BY

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With 25 Illustrations, including 1 Plate.

THIRD EDITION



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PREFACE TO FIRST EDITION.

IN connection with experimental work in Physiology, Chemistry, and Hygiene, and in the investigation of mine air, products of combustion, etc., methods of air and gas analysis which are both rapid and accurate are greatly needed. This short book contains a description of methods—most of them more or less original—which I have found useful in this class of work. The book is in no sense a complete treatise on gas analysis. The methods described are only such as are designed to meet everyday needs in connection with the analysis of air and comparatively simple gas mixtures. Nearly all the original methods were first described in papers in the *Journal of Physiology*, *Journal of Hygiene*, *Transactions of the Institution of Mining Engineers*, or in Bluebooks; and several of them were collected in *The Investigation of Mine Air*, now out of print. The descriptions are given in considerable detail, as attention to small matters of detail is often of much importance; and a number of improvements, the result of extended experience, and not described in the original papers, are embodied in the text.

J. S. H.

January 1912.

PREFACE TO SECOND EDITION.

THE present edition has been revised throughout, and descriptions of several new methods have been added.

September 1918.

Reprinted for Third Edition, 1920.

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METHODS OF AIR ANALYSIS.

THE COLLECTION OF SAMPLES OF AIR.

IN any investigation of the composition of air the first step is the collection of a sample for analysis. In collecting a sample it is necessary to take care (1) that the sample is not altered in the process of collection or storage, (2) that the vessel containing the sample is thoroughly air-tight. It is also very desirable to use a vessel which can be handled conveniently, and from which a portion of the sample can be transferred conveniently to the gas-analysis apparatus.

The simplest case is where the sample can be collected directly in the burette of the gas-analysis apparatus. This method can be used with a portable apparatus for the analysis of air at any point, for instance, in an ordinary room, an air-way in a mine, an experimental respiration chamber, etc. The burette is filled with mercury in the ordinary way described below, the tap of the burette closed, and the mercury reservoir lowered, so that on opening the tap at the point where a sample of air is wanted the mercury runs out of the burette and

air is drawn in. The rate of outflow of the mercury can be regulated by a screw clip on the rubber tubing connecting the gas-burette with the reservoir, so that the collection of the sample is spread over some time; and during the collection the apparatus, if it is portable, may be carried about in the room. By these means a fair average sample may be obtained in cases where the air is not uniform in composition. In an experimental chamber uniformity of composition may be ensured by thoroughly mixing the air with an electric fan. Care must always, of course, be taken that the sample is not directly contaminated by the expired air of the person taking the sample.

In other cases it is necessary to collect samples of the air for subsequent analysis at some convenient time and place. Where a large volume of air has to be examined, as in a room, or a mine air-way or working place, the samples are best collected in ordinary three-ounce bottles of clear glass with properly ground glass stoppers. These bottles hold about 90 c.c., which is enough for several ordinary analyses, so that any determination can be repeated if necessary. They are cheap, easily obtained, and suitable for sending by post where necessary. A number of them can easily be carried about. The stopper of each bottle is greased with vaseline, and after the sample is taken should be turned round until no air-channels are visible in the vaseline. The stopper is held in position by a fairly stout elastic band held over it, and a gummed label is placed on the bottle, as shown in fig. 1.

The bottles must be dry and clean. They should be cleaned with a brush, rinsed with clean (preferably distilled) water, and dried completely by leaving them on some warm place or blowing them out with air while they are kept warm. Alcohol, ether, etc., should not be used for drying them, as traces of ether may remain and cause serious error. If a bottle is wet and dirty, an appreciable amount of carbon dioxide may appear, and of oxygen disappear, by bacterial action. To quote an example, after four days the carbon dioxide had increased by .05 per cent., and after ten days by .12 per cent., in a wet and dirty bottle. If, on the other hand, the bottle is wet and clean the carbon dioxide gradually disappears, as it is absorbed by alkali dissolved out of the glass by the water. For instance, the whole of the carbon dioxide (.03 per cent.) in a sample of pure atmospheric air had disappeared in a wet bottle in twelve days.



FIG. 1.—Sampling Bottle.

The rubber band is specially desirable for samples taken in mines, as the stopper might otherwise be blown out in consequence of diminution of atmospheric pressure during the ascent to the surface. Bottles with wide glass stoppers should not be used, partly because a wide stopper is more liable to be blown out, and partly because great inconvenience may be caused, owing to the fact that a wide-mouthed bottle will not fit into the mercury

trough used in transferring the air from the bottle into the gas-analysis apparatus. For the same reason large bottles are very unsuitable, apart altogether from the great inconvenience in carrying them about.

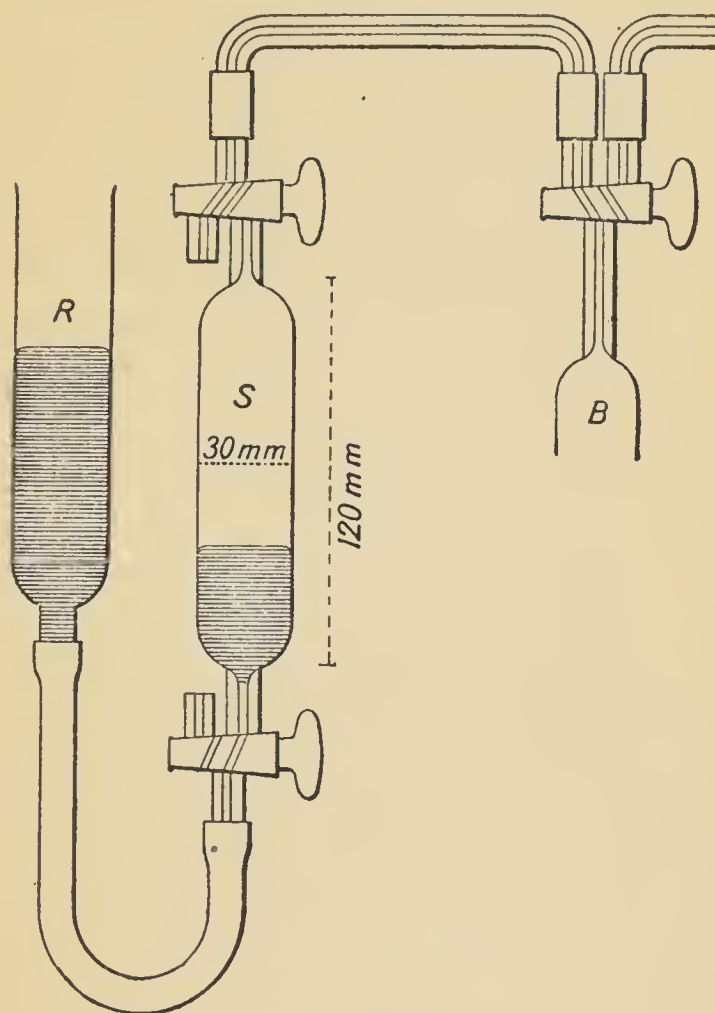
The sample is collected as follows. One end of a piece of rubber tubing about two or three feet long, and $\frac{1}{8}$ or $\frac{1}{4}$ inch in internal diameter, is introduced into the bottle to the bottom, the other end of the tube being held in the mouth. A deep breath of air is then sucked in through the tube. The bottle is in this way very thoroughly washed out by the incoming air, since the volume of air sucked through will be more than ten times as great as the capacity of the bottle. The tube is removed while the air is still being sucked up, so as to avoid any risk of breath passing backwards into the bottle. The stopper is then inserted, turned round, and secured as already described, and the particulars written on the label.

When the gas to be examined is issuing from a pipe or bore-hole a sample may be obtained by arranging a piece of rubber or bent glass tube so as to pass through a plug of clay inserted in the end of the pipe. The free end of the tube is then placed in the bottle, which must be inverted if the issuing gas is lighter than air. The stopper must, of course, be inserted as soon as the tube is withdrawn.

When samples are collected over water, or by emptying vessels of water, the carbon dioxide percentage is not reliable, as the water or wet bottle may have absorbed some of the gas, or the water may have given off carbon dioxide to the air. Samples collected in metallic vessels

are unreliable as regards oxygen, if, as is often the case, oxidation of the metal is going on inside.

In physiological work, investigation of furnace gases,



S = Sampling tube.
R = Mercury reservoir.
B = Gas-burette.

FIG. 2.—Sampling Tube, showing Mode of Connecting with Burette.

etc., the sample has often to be exhausted from a tube or other small space. In all such cases the form of sampling tube shown in fig. 2 is very convenient. It has a capacity of about 70 c.c., and is provided with a

three-way tap at each end, the taps being arranged as shown in the figure. In taking a sample the sampling tube may be connected by a rubber tube with the mercury reservoir R in the manner shown. The sampling tube is then filled with mercury by raising R. The upper tap and connecting tubing to the point from which the gas has to be drawn are also filled with mercury. The upper tap is then closed, and the reservoir R lowered. On opening the upper tap the mercury flows into R, and the sampling tube is filled with the gas. By regulating the lower tap the process of filling may be made very slow, if this is required. Another method is to exhaust the sampling tube S first. This is done by lowering R more than 30 inches below S, so that when the upper tap is closed S is completely exhausted. Both taps are then closed and S is disconnected, ready for use. Any connection between S and the source of the gas should either be filled with mercury or with the gas to be examined. Some of this gas can be sucked through these connections by means of a piece of rubber tube attached to the free limb of the upper three-way tap, which is then turned so as to connect with the vacuous space in S, which is instantly filled with the gas. A series of samples can be taken very conveniently by means of vacuous sampling tubes. The gas is also very easy to transfer to the gas-analysis apparatus by the arrangement shown in fig. 2 and described below.

When the gas to be analysed and measured is delivered from a mercury pump, as in blood-gas analyses, etc., the

form of receiver shown in fig. 3 is very convenient. This receiver is first filled with mercury (including the bore of the tap), and then placed over the delivery tube of the pump in a mercury vessel, so as to receive the gas, which can afterwards

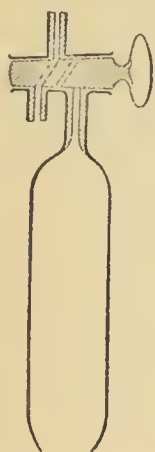


FIG. 3. — Bohr's Gas Receiver, slightly modified.

be transferred very easily to the gas-analysis apparatus.

For collecting a sample of gas or air at an even rate over any required period of time, Huntly¹ has devised the form of sampling tube shown in fig. 4. It will be

seen from the construction of this tube that the gas is sucked in under a constant pressure until the mercury falls to within half an inch of the lower end of the tube. The rate of inflow was found to be constant within 1 per cent. In other respects, the construction and the precautions needed are the same as in the case of the sampling tube shown in fig. 2.

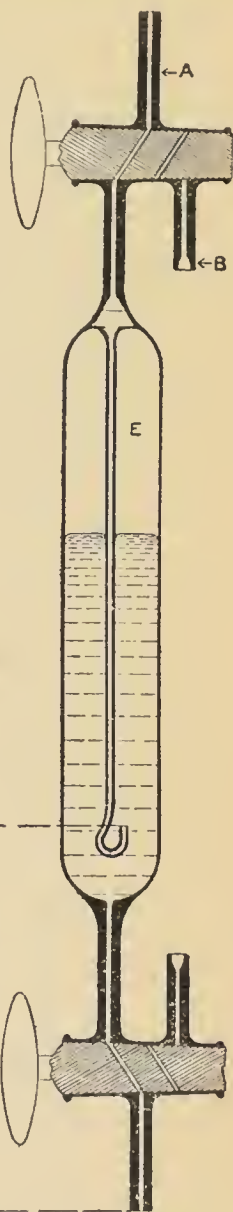


FIG. 4. — Huntly's Gas Sampling Tube.

¹ *Journ. Soc. Chem. Industry*, 1910, p. 312.

When samples are sent for analysis to an analyst it may save much trouble if he is informed as to the circumstances under which the sample was taken. If, for instance, the sample is one of mine air and he has been informed that a lamp would burn at the point where the sample was taken, he can proceed with the analysis without preliminary tests; and similarly if he knows that the sample is from a blower of fire-damp. He should also be informed if there is any reason to suspect the presence of small percentages of carbon monoxide or other unusual gas in small quantity.

APPARATUS FOR GENERAL AIR ANALYSIS AND GAS ANALYSIS.

Two forms of gas-analysis apparatus, the same in principle, will be described. The larger form, which gives the more accurate results, is suited only for use in a laboratory where it can be set up permanently. The smaller form can be moved about easily, and may be used at any place where it is required. For ordinary purposes, even in laboratory work, it has proved the more useful of the two, though it was originally designed for work outside a laboratory. The method of using the larger apparatus will be described first; but, allowing for differences in detail, the description applies also to the smaller apparatus.

Description of Large Apparatus¹ (fig. 5).—The sample of air is measured in a gas-burette (A, fig. 4) about 32 inches (800 mm.) long, provided at the top with a three-way tap. The upper wide part is about 1 inch (25 mm.) in diameter, and has a capacity of about 15 c.c. The graduation, which is to .01 c.c., extends down the narrow part, which is 3.5 mm. in bore, from about 15 to 21 c.c., the capacity being measured from

¹ The various special forms of apparatus described in this book are made by Messrs Siebe, Gorman & Co., 187 Westminster Bridge Road, London. The apparatus in its original form was described in the *Journal of Physiology*, vol. xxii., 1898.

the tap (not including its bore) to the upper surface of the mercury. There are also marks at the first 5 c.c. on the wide part. With such a burette it is possible to read without the aid of a telescope to within an error of .001 c.c. A magnifying glass is desirable, however, and a good light behind the burette is also needed. The burette must, of course, be most carefully graduated by the maker, and may be checked by reversing the burette, filling with mercury, and weighing out successive portions of about 1 c.c., accurately read off on the burette. The mercury is allowed to flow out through the tap into a weighed vessel, any hanging droplet of mercury being carefully brushed down before each weighing. In estimating the volume from the tap to the first graduation it is necessary to add .004 c.c. to the volume calculated from the weight of mercury which flows out between these points, as the mercury has its convexity towards the tap when the burette is in its natural position. During the whole operation the temperature of the mercury in the burette must, of course, be kept constant. The burette may be still more exactly calibrated if a tap is temporarily fused on the lower end: for the calibration can then be done with the instrument in its natural position. It can also be moistened internally with water, just as when it is in actual use. Another easy method of practically testing the calibration of the burette will be described below. An irregularly calibrated burette is a source of endless trouble, and should be rejected.

Surrounding the gas-burette is a water-jacket, which is about $2\frac{1}{2}$ inches in diameter, and is supported by an ordinary clamp fixed on a retort-stand, which is itself clamped to the front of the table. The water in the jacket can be mixed by blowing air through a glass tube passing to the bottom. The gas-burette is connected by means of thick-walled rubber tubing of about 3 mm. bore with the levelling-tube B, which is about 15 mm. in bore. By raising or lowering this tube, which is held by a spring clamp fixed to the retort-stand and opening easily, gas is expelled from or drawn into the burette, and the pressure in the latter adjusted.

One of the three-way connections of the tap on the burette is used for taking in the sample, and the other connects the burette with absorption and combustion pipettes, which are arranged as shown. The connecting pieces are of 2 mm. bore, and are joined together by pieces of thick and soft red rubber tubing of the best quality, clean and smooth inside.

The absorption pipettes E and F are about 100 mm. long and 30 mm. in internal diameter. F is filled with glass tubes in order to increase the absorbing surface. The tubing leading up from them must have a bore of about 2 mm. (1.8 to 2.2 mm.). E is filled with caustic potash or soda solution (about 10 per cent.¹), and is connected with the movable reservoir S by black rubber tubing, as black rubber is less apt than other kinds to give off sulphide to the potash solution. The alkaline pyro-

¹ If gases, such as nitrous oxide, which are very soluble in water, but are not intended to be absorbed by the soda, are present, a saturated solution should be used to prevent the solution.

gallate solution filling F is made as follows. In 100 c.c. of nearly saturated solution (the specific gravity of which should be 1.55) of caustic potash 10 grammes of pyrogallie acid are dissolved in a bottle with a greased stopper. This solution is introduced into F through the tube K by means of a large pipette, the open end of K being afterwards securely closed by a piece of glass rod pushed well in. G and H, which have each a capacity of about 30 c.c., are partly filled with some of the strong potash solution. This not only protects the pyrogallate solution from the oxygen of the air, but also prevents the solution from becoming gradually diluted with water, as happens when plain water is placed in G and H.

The solutions last for a very large number of analyses (more than one hundred). When it is found that the oxygen absorption is becoming sluggish the pyrogallate solution should be changed. By mere standing in the absorption pipette it never deteriorates, which is a great advantage. It also has the advantage over phosphorus that it acts equally well whatever the oxygen percentage may be, and is very little affected by temperature. It is important that the solution should be made exactly in the manner described. If the potash is weaker the absorption of oxygen is much slower, and with some mixtures carbon monoxide may be formed. The strong solution has the further advantage that its coefficient of absorption for gases is very low. It produces no measurable carbon monoxide, and is in every way a most perfect and convenient absorbent for oxygen. When freshly

made it absorbs much less rapidly than after it has stood for some time. A stock of it should therefore be kept for recharging the pipette.

The pressure in the burette is adjusted by using the potash pipette as a pressure-gauge, and bringing the potash before every reading of the burette exactly to the mark M. As the potash solution has only about one-tenth of the specific gravity of mercury, and with a tube of .2 mm. bore the level can be adjusted very accurately, it is evident that the pressure can be adjusted with great exactitude.

In order to make the readings of the burette entirely independent of changes in temperature, barometric pressure, and percentage of moisture during the analysis, a control-tube N, which stands beside the burette in the water-jacket, is employed. The connecting tubes from N are of the same diameter and about the same length as those from the gas-burette; and a three-way tap at P makes it possible to equalise the pressure in N with that of the atmosphere. By means of the T-tube O the potash solution is brought into connection with N. At the beginning of the analysis the potash is adjusted to the mark R by raising or lowering the potash reservoir S, P being open to the air. P is now turned so that the control tube is connected with the potash tube only, and is not again opened till the analysis is complete. Each time a reading of the burette is made the potash is brought to the mark R by raising or lowering S. The potash in the absorption pipette is then brought to the corresponding mark M by adjusting the levelling-tube. The readings of the

burette are thus compensated by mechanical means for variations of temperature and barometric pressure during the analysis, so that temperature and pressure may be disregarded. The lower part of the control tube is kept full of water, and particular care must also be taken that the burette is kept moistened sufficiently to make its inner surface wet without fouling the mercury meniscus, so that the air in the burette and control tube is always saturated. The water used for moistening the inside of the burette should be slightly acidified with sulphuric acid in case alkali from the glass should render it alkaline; and occasional re-moistening is also necessary. It is easy to see whether the burette is moist. The acidified water is introduced through the free limb of the tap, any excess being afterwards expelled by raising the levelling-tube. If the burette is allowed to become dry, very appreciable errors are produced. A sample of pure air will, for instance, probably increase in volume when passed over into the potash pipette, as the air will take up more moisture than it loses of CO_2 in contact with the potash solution.

The use of a control tube in gas analysis was first described by Williamson and Russell,¹ who employed a mercury pressure gauge. The same principle in a much improved form was applied in Petterson's apparatus,² in which the movement of a drop of oil in a horizontal tube connecting the burette with the control tube is used as a pressure indicator, and extreme accuracy in the

¹ *Journ. of Chemical Society*, 1868, p. 238.

² *Zeitschr. f. analyt. Chemie*, vol. xxv. pp. 467, 479.

adjustment of pressure is thus obtained. The Petterson apparatus is, however, difficult to manage, and the dead space in the glass tube connecting the burette with the pressure gauge cannot be washed out.

The combustion pipette T, which is filled with mercury, is about 80 mm. long by 30 mm. in internal diameter, and contains a spiral of three turns of very fine platinum wire. The current is led to the spiral through the two glass tubes shown. A piece of stout platinum wire, passing through the sealed ends of each of these tubes, carries the current. The upper ends of the two stout wires are connected with the spiral, while the lower ends are connected through copper wires with a small accumulator or other source of current. The combustion pipette is closed below by a cork soaked in paraffin, so that it is always easy to open the pipette (after warming the glass, so as to melt the paraffin) if the spiral has fused, and it is necessary to renew it. The cork should be secured by wiring, to prevent its being driven out by an accidental explosion in the pipette.

To heat the spiral, cells giving about four volts are needed. A rheostat is also required, so that the current can be gradually increased until the spiral reaches a bright white heat. A lower heat is sufficient in burning hydrogen or carbon monoxide, but a white heat is needed for methane, and the heat should be increased cautiously, as otherwise the wire may fuse owing to the extra heat produced at first by the combustion. An ordinary hand electric lamp, with a small rheostat arranged on the top, as shown in fig. 5, answers very well. A small

double accumulator, such as is used on motor-cars, is equally suitable: dry cells of sufficient size will also answer, or bichromate batteries. But perhaps the most convenient plan is to use the ordinary lighting current,

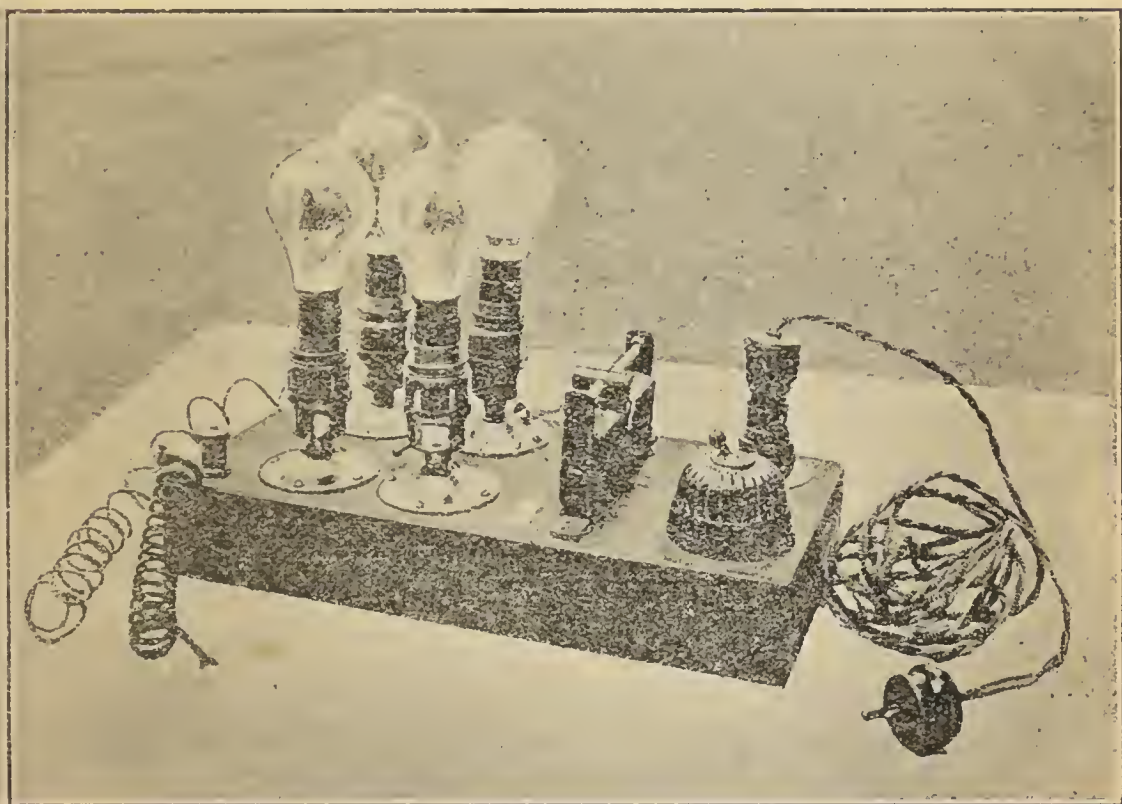


FIG. 6.—Rheostat with Lamp Resistances.

with a suitable lamp resistance and rheostat, as shown in fig. 6.

The method of burning combustible gases by means of a heated platinum wire was first introduced by Coquillion¹ for the estimation of methane in mine air. It presents the advantage that where the volume of combustible gas present is less than sufficient to form an

¹ *Comptes Rendus*, vol. lxxxiv. p. 458, 1877.

explosive mixture with air or oxygen it is not necessary to add hydrogen or detonating gas, as in the older methods of analysis, since, however small the proportion of combustible gas present may be, the combustion occurs very readily in presence of the heated platinum. The addition of pure hydrogen, oxygen, etc., can thus be entirely done away with in gas analysis, and only air need be added when oxygen is required for the combustion. Since the composition of the outside air is practically constant, except during fogs in large towns, this is a great advantage, as errors arising from slightly impure oxygen, hydrogen, etc., or from the burning of nitrogen in exploding the sample, are entirely avoided, as well as the trouble of preparing pure oxygen, hydrogen, and detonating gas.

By the use of the control tube, pipettes permanently connected for absorption or combustion, the platinum spiral, and the special form of burette, with mercury as a confining liquid, the time required for accurate analysis of air and other simple gas mixtures is enormously reduced as compared with that needed by the older classical methods, and many troublesome calculations are dispensed with. The accuracy attained is also greater. The apparatus is not suited for the analysis of very complex gas mixtures, but such analyses are but seldom required.

Transference of Sample to Gas-burette.—Before taking a sample of the gas into the gas-burette for analysis it is necessary to see that the connecting tubing to the absorption and combustion pipettes is free from

any gas which has to be directly determined, or which might interfere with its determination. For instance, if oxygen has to be determined there must be no oxygen in the connections, or if methane has to be determined there must be no combustible gas in the connections. As a general rule the connections must be filled with nitrogen. A supply of this will probably have been left at the end of the previous analysis; and this nitrogen is always kept, so that the apparatus is ready to start on the new analysis. If, however, it has stood for some hours the connections should be washed through with the gas, so that any oxygen which has diffused in through the rubber joints (as happens if the apparatus stands for long) may be absorbed by the pyrogallate solution. If no nitrogen was left from the previous analysis some air may be taken in, and nitrogen prepared from it. If only carbon dioxide, or some combustible gas, has to be determined, the presence of oxygen in the connections does not matter. The next step is to bring the pyrogallate, mercury, and potash to the marks D, V, R, and M on the gauges of the absorption and combustion pipettes and of the control tube. The tap connecting with the control tube is then closed to the outside air.

If the sample is in a bottle the mercury trough shown in fig. 7 is needed. It is made, either solid, or of two slabs of hard wood, which are so cut out that when they are screwed together a narrow slit open at the top is left between them. At one end of the upper part the slit expands into a rectangular space $2\frac{1}{2}$ inches long by

1 $\frac{1}{4}$ inches wide and 1 $\frac{1}{2}$ inches deep, in which the neck of the bottle is received. The slit itself is $\frac{1}{4}$ inch wide by 6 inches long and 4 inches deep. The trough, if

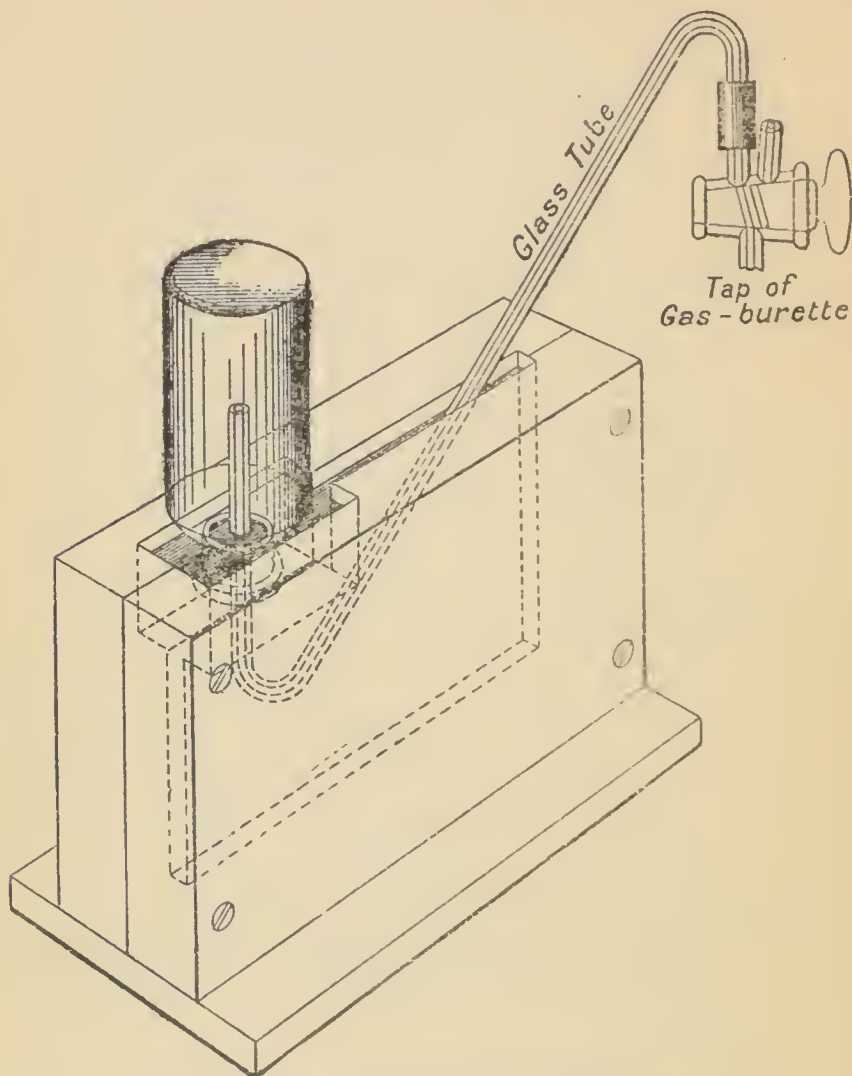


FIG. 7.—Mercury Trough for Sample-Bottles.

made in two pieces, is rendered tight by a layer of marine glue.

A piece of narrow-bored glass tube, bent as shown in fig. 7, is used for transferring the sample. After the

gauges of the burette have been adjusted in the manner already described, the tap of the burette is opened towards the outside, and the contained gas expelled through the bent tube attached to the top of the burette, mercury being allowed to follow until the bent tube is completely filled with it. The tap of

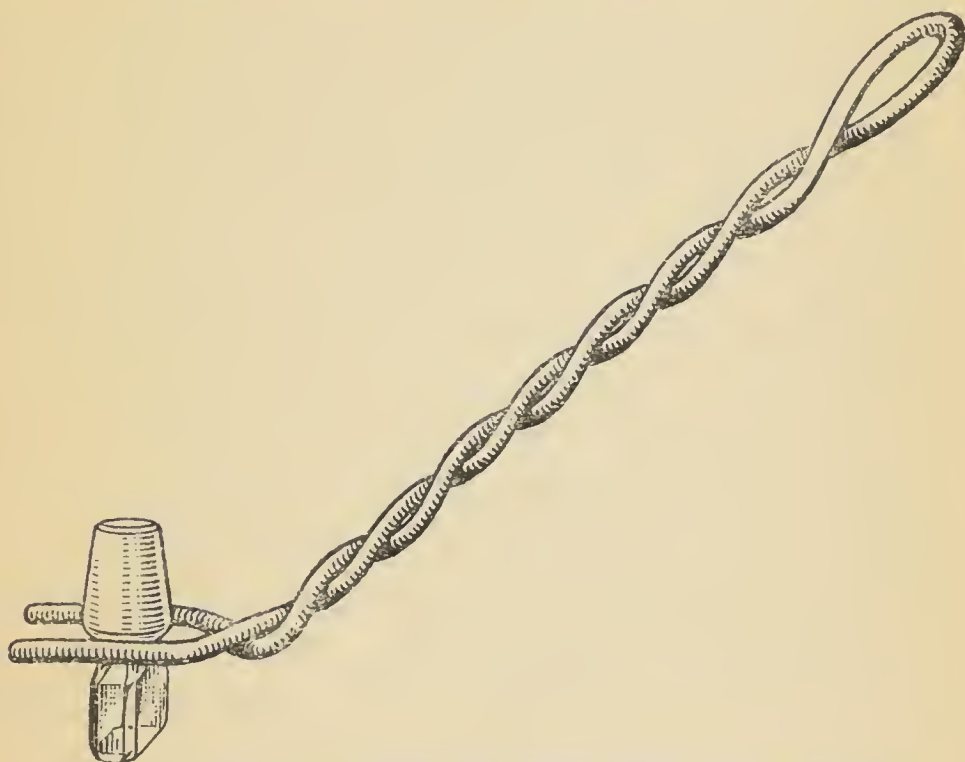


FIG. 8.—Fork for Manipulating Glass Stoppers under Mercury.

the burette is then closed and the levelling-tube lowered so as to produce a negative pressure in the burette.

The next step is to turn round the stopper of the sample bottle, so as to loosen it if it is tight. The neck is then inverted under mercury in the trough, and the stopper is removed with the help of a fork (fig. 8) made from stout iron wire.¹ This grasps the neck of the

¹ The use of a fork was suggested by Fleet-Surgeon Rees, R.N.

stopper, which can then be easily removed or replaced without letting any air into the bottle. If the stopper is removed under water, which may sometimes be necessary with an awkwardly shaped stopper, the bottle should first be slightly warmed, so as to ensure that the pressure inside is positive, and no water enters; the neck is then at once closed by the middle finger and the bottle transferred to the mercury trough.

The free end of the bent tube is now depressed below the mercury level and introduced into the neck of the bottle, and the tap of the burette is turned so as to allow the sample to be sucked into the burette. During this operation the bottle should be steadied with one hand; as soon as the sample is sucked in the bottle becomes steady owing to the fact that mercury has been sucked up inside it, and support by the hand is no longer necessary. More than 20 c.c. of the sample should in most cases be taken in, after which the tap is completely closed by a quarter-turn. The pressure inside the burette is now negative, and must be roughly adjusted to atmospheric pressure by raising the leveling-tube. It is then safe to turn the tap so as to connect the burette with the potash pipette. If there was much negative pressure in the burette the potash might be sucked over on opening the tap. A positive pressure might, on the other hand, drive some of the sample into the potash pipette before the first reading was taken.

The general procedure required when the sample is contained in a sampling tube will be evident from fig. 2.

The sampling tube is connected with the mercury reservoir, any air-bubbles being driven out through the free limb of the lower three-way tap. The burette is also connected with one end of the sampling tube by a piece of glass tubing of 2 mm. bore, and bent as shown in the figure. The gas in the burette is then expelled through the free limb of the three-way tap on the upper end of the sampling tube, and mercury is driven over so as to fill the connections up to this tap. Any mercury which escapes can be caught in a small test-tube hung from the barrel of the tap by a wire. The tap on the sampling tube is then completely closed, and the levelling-tube depressed, so that any leakage in the connections, or the presence of any air-bubble, can be detected at once. An air-bubble sometimes sticks at the rubber joint between the connecting tube and sampling tube. To expel this the easiest plan may be to pinch one side of the rubber so as to allow a channel of escape for the bubble. Soft, black rubber should therefore be used in making the joint. When everything is ready the levelling-tube is lowered and the taps opened so that a sample is sucked into the burette. The pressure inside the burette can then be adjusted to normal by raising or lowering the reservoir R, or the levelling-tube.

If the sampling tube has only plain taps, the glass tubing above the tap must be filled with mercury by means of a fine glass pipette before the sampling tube is joined to the connecting tube. The air is then expelled from the latter after pinching one side of the rubber joint so as to open a channel. The free end of the lower

tap must also be filled with mercury before connecting with the rubber tube attached to R. It is then possible to make a connection without including any air.

Process of Analysis.—The procedure to be adopted will evidently depend on the composition of the sample, and on what constituents it is necessary to determine. The qualitative, and approximate quantitative, composition of the sample will generally be known beforehand, and will thus be a guide. A series of examples will illustrate the various procedures.

Let us first take the simple, but extremely common, case, in which the sample is known to contain nothing but carbon dioxide, oxygen, and nitrogen. A sample of expired air collected in a bag during a respiration experiment will serve as an example.

After the sample has been taken into the burette and the pressure roughly equalised, as already described, the next step is to open the tap of the burette so as to connect with the potash pipette. The level at which the potash stood had previously been adjusted exactly to the mark (M, fig. 5) with the connections to the potash and pyrogallate pipettes filled with nitrogen, as also already described. On opening the tap this level will probably be slightly disturbed, and the potash level at R may also have shifted a little. By raising or lowering S the potash level is exactly adjusted at the mark R, and by raising or lowering the levelling-tube the potash level at M is also exactly adjusted. Before doing this, however, some air should be blown through the mixing tube, so as to make the temperature even in the water-jacket. The

level of the top of the mercury in the burette is now read off exactly in the burette to .002 c.c. with the help of a lens. The air is then driven into the potash pipette by raising the levelling-tube, which is released from the spring clip and held in the hand. The mercury is allowed to pass up in the burette to the level of the neck, but not further. The air is then brought back till the potash rises to about M, and this process is repeated about four times, after which all the carbon dioxide will have been absorbed, as shown by the fact that no further diminution of volume occurs. The water in the jacket is again mixed, and the two potash levels adjusted, and a second reading is taken, which shows the volume of carbon dioxide in the sample. The burette is now connected with the pyrogallate pipette, and the air driven over into this, and returned once or twice, after which nearly all the oxygen will have been absorbed. Some oxygen is, however, left in the connection between M and the tap, so this connection is washed out by passing the gas into the potash pipette and back, and then into the pyrogallate pipette and back twice. The washing-out is afterwards repeated to remove the last traces of oxygen. The levels at D, R, and M are then adjusted as previously, and a reading again taken, which shows the volume of oxygen absorbed. If any doubt remains as to the completeness of the absorption of oxygen, the gas should be returned once more to the pyrogallate pipette. If absorption was complete, the reading afterwards should be exactly the same.

The following is an example of the figures obtained :—

Volume of expired air taken	20.612	
After CO ₂ absorbed	19.846	
		<hr/>
∴ CO ₂	=	0.766 = 3.72 per cent.
After O ₂ absorbed	16.424	
		<hr/>
∴ O ₂	=	<u>3.422</u> = 16.60 per cent.

As it was known that the sample contained only oxygen, carbon dioxide, and nitrogen (including argon), the latter gas may be calculated by difference, so that the result of the analysis is :—

Carbon dioxide	3.72
Oxygen	16.60
Nitrogen	79.68
	<hr/>
	<u>100.00</u>

In this statement of the result no account is taken of errors in the burette. Appreciable errors are nearly always present, however, and must be corrected for. The method of correcting for these errors will be discussed later.

Let us now suppose that the sample contained more than 30 per cent. of oxygen, or carbon dioxide, or of both gases together. It is clear that if the burette has been filled with the sample at first, it will not be possible to get any reading after absorption of the oxygen, as the mercury level will be above the graduations. In such a case sufficient nitrogen to fill the burette to the top

of the graduation must be kept from the last analysis, and only enough of the sample taken in to fill up the burette to near the bottom of the graduation. The analysis can then be done without difficulty. We may take as an example the analysis of a sample of commercial oxygen from a steel cylinder. The volume of nitrogen retained from the last analysis, and measured with the usual precautions, was 15.146. This was then shunted completely into the pyrogallate pipette. About 5 c.c. of the sample were then taken into the burette, the amount being roughly estimated by the coarse graduations on the upper part of the bulb of the burette. The nitrogen was then drawn back from the pyrogallate pipette and the total volume of gas was now measured, and found to be 20.202, so that 5.056 c.c. of the sample had been taken in. The analysis of this was then proceeded with in the ordinary way, with the following results:—

Nitrogen in burette	.	.	15.146	
+ sample taken in	.	.	20.202	
			<hr/>	
∴ sample	=		5.056	
After CO ₂ absorbed	.	.	20.202	
			<hr/>	
∴ CO ₂	=		0.000	= 0.00 per cent.
After O ₂ absorbed	.	.	15.284	
			<hr/>	
∴ O ₂	=		<u>4.918</u>	= 97.27 per cent.

In this case it is clear that the degree of accuracy of the analysis will be less than when the whole burette

has been filled with the sample; for the readings can only be made to one part in 5000 (or 0.02 per cent.), instead of one part in 20,000. On the other hand, there will probably be no correction for error in the burette, as will be explained below.

The next case is that of air containing some one combustible gas, as well as carbon dioxide, oxygen, and nitrogen. The following analysis of air from a return air-way in a colliery is a typical example. As the sample was collected at a place where lamps burned, it was known that the air contained sufficient oxygen to burn any methane which was present.

Before the analysis the connections of the combustion pipette, as well as of the absorption pipettes, were filled with nitrogen. About 20 c.c. of the sample were taken in and measured; the carbon dioxide was then absorbed and the residue measured. The gas was then passed into the combustion pipette, the spiral heated white hot, and the gas passed backwards and forwards over the spiral several times. After waiting a short time for the glass to cool, the mercury in the combustion tube was re-adjusted to the mark, and the gas measured in order to obtain the contraction on combustion. The CO_2 formed by the combustion was then absorbed in the potash pipette, care being taken to wash out the combustion pipette, so as to remove any CO_2 left in the connections. After again measuring to obtain the volume of CO_2 formed, the gas was passed over the spiral in order to burn the fraction which had escaped the first combustion, owing to the existence of the small

dead space in the connection to the potash pipette. Without waiting to obtain the second contraction, the CO_2 formed was absorbed. The total contraction was then measured. After this the oxygen remaining in the sample was absorbed and the residue of nitrogen measured. The actual measurements were as follows:—

Volume of air taken	.	.	20.024
After CO_2 absorbed	.	.	19.982
<hr/>			
$\therefore \text{CO}_2$		=	0.042 = 0.21 per cent.
After combustion	.	.	19.480
\therefore contraction		=	.502
After CO_2 absorbed	.	.	19.230
<hr/>			
$\therefore \text{CO}_2$ absorbed		=	0.250
After second combustion and			
CO_2 absorption	.	.	19.206
<hr/>			
\therefore difference		=	0.024
After O_2 absorbed	.	.	15.642
<hr/>			
\therefore oxygen absorbed		=	<u>3.564</u>

In this sample the only combustible gas present was methane (CH_4).¹ This is indicated, though not conclusively proved, by the fact that the contraction on combustion was, within the error of analysis, exactly double the carbon dioxide formed. A mixture of equal parts of carbon monoxide and hydrogen, or ethane

¹ In the writer's experience the "fire-damp" of mines in this country has almost invariably been nothing but methane.

and hydrogen, would also give a contraction which was double the carbon dioxide formed; but such mixtures do not occur in a mine, so their possible existence need not be considered, and we may assume that the combustion took place in accordance with the equation,



As the water condenses, the volume of CH_4 present is evidently half the contraction on combustion, or one-third of the total diminution of volume after all the CO_2 has been absorbed. This total diminution was $\cdot 502 + \cdot 250 + \cdot 024 = \cdot 776$, and this $\times \frac{1}{3} = \cdot 259$, which is 1·29 per cent. of the volume of air taken.

The oxygen which disappeared in the combustion was evidently double the volume of methane, or $\cdot 776 \times \frac{2}{3} = \cdot 517$, and the oxygen left was 3·564, so that the total oxygen present in the air taken was $\cdot 517 + 3\cdot 564 = 4\cdot 081$, or 20·38 per cent.

The result of the analysis was thus:—

Oxygen	20·38
Carbon dioxide . .	0·21
Methane	1·29
Nitrogen	78·12
	<hr/>
	100 00
	<hr/>

It is often only the methane percentage which is required in an analysis of mine air. In such a case it is only necessary to measure the volume of air taken, pass it directly to the combustion pipette, and then measure

again. The methane present is equal to half the contraction.

If the sample does not contain, or is not known to contain, sufficient oxygen to burn the combustible gas, it must first be diluted with a sufficiency of air. The degree of dilution necessary will depend on the nature and amount of the gas known to be actually or possibly present; and in any case sufficient oxygen must be present in the air to burn completely the maximum of combustible gas which might be present. As a general rule the dilution should be sufficient to ensure that the gas will burn quietly without exploding in the combustion pipette, as, unless the cork of the latter is very firmly secured, it might be loosened by a sharp explosion. To form a mixture which is just explosive, about 16 per cent. of carbon monoxide, 9 per cent. of hydrogen, 6 per cent. of methane, 4 per cent. of ethylene, 3 per cent. of acetylene, and $2\frac{1}{2}$ per cent. of benzene or pentane, must be present; and for commonly occurring mixed gases the corresponding limits are about 12 per cent. for water-gas, and 8 per cent. for coal-gas. The sample ought, therefore, to be so diluted with air that the percentage of the combustible gas shall not exceed these limits. Thus, if a sample of carbon monoxide is being analysed for purity, as may be frequently necessary in certain kinds of physiological work, not more than 3 c.c. of gas should be taken to 20 c.c. of the mixture of air; or if a sample of fire-damp from a blower or cavity in the roof were being examined, not more than 1.2 c.c. should be taken to 20 c.c. of the mixture, since the gas

might be almost pure methane. It may, of course, turn out that the combustible gas was very dilute. In such a case a second analysis should be done if much exactitude is necessary—particularly if the first analysis showed that the sample could be analysed without any dilution. If, however, anything is known about the sample, or any proper description has been given by the person who may have sent it, a second analysis is seldom needed.

The following analysis of gas issuing through a pipe from behind a stopping in a coal-mine will serve as an example. From indications of the safety-lamps it was known that this gas contained much fire-damp and was possibly almost pure fire-damp. Sufficient pure outside air was first taken in, freed from CO_2 , measured, and shunted into the potash pipette. About 1 c.c. of the gas was then taken in and roughly measured by the coarse graduations, the air added, and the analysis then proceeded with as usual, the results being as follows:—

Air (freed from CO_2) . . .	18.892
+ sample taken in . . .	20.010
	<hr/>
\therefore sample . . .	= 1.118
After CO_2 absorbed . . .	19.976
	<hr/>
$\therefore \text{CO}_2$. . .	= 0.034 = 3.0 per cent.
After first combustion . . .	18.824
	<hr/>
\therefore contraction . . .	= 1.152
After CO_2 absorbed . . .	18.248
	<hr/>
$\therefore \text{CO}_2$ formed . . .	= 0.576

After second combustion and ab-			
sorption of CO ₂	.	.	18·196
			<hr/>
∴ difference			= 0·052
After oxygen absorbed	.	.	15·360
			<hr/>
∴ oxygen which remained			= <u>2·836</u>

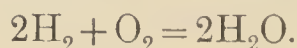
As the contraction was exactly double the CO₂ formed, the combustible gas was evidently pure methane. The total diminution in volume after combustion and absorption of CO₂ was $1·152 + 0·576 + 0·052$, or $1·780$, and this $\times \frac{1}{2}$ gives the volume of methane, which is $0·593$, or $53·0$ per cent. of the volume of gas taken. With the burette used, the oxygen percentage in pure outside air free from CO₂ was $21·01$ per cent. Hence the volume of oxygen in the $18·892$ c.c. of air taken was $3·969$ c.c. But $1·187$ c.c. of oxygen were used up in the combustion, and the excess over at the end was $2·836$ c.c.—total $4·023$ c.c. Hence $4·023 - 3·969 = 0·054$ c.c. was present in the sample, or $4·8$ per cent. The result of the analysis was therefore as follows:—

Carbon dioxide	3·0
Oxygen	4·8
Methane	53·0
Nitrogen	39·2
	<hr/>
	<u>100·0</u>

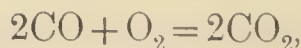
It will be noticed that the percentages are calculated to $\cdot 1$ per cent., and not to $\cdot 01$ per cent., as in the examples given above. It would be useless to calculate

the results further, as the figures would be meaningless, since the graduation of the burette and other experimental errors do not permit of a division of 1.118 c.c. (the volume taken) into smaller parts than one-thousandth. The common practice of putting wholly meaningless figures into the results of an analysis is greatly to be deprecated. If it were of any importance to obtain more accurate results for the carbon dioxide and oxygen, a determination of them could be made with 20 c.c. of the sample; or a second analysis could be done in the same way as the first, but with double as much of the sample, since only about half the gas was methane.

The above examples will serve to illustrate the general method of determining a combustible gas when one such gas only is present in the sample; but, of course, the ratio of contraction on combustion to carbon dioxide formed will vary with the kind of combustible gas present. If, for instance, this gas is hydrogen, the combustion will take place in accordance with the equation



The contraction on combustion will thus be $1\frac{1}{2}$ the volume of hydrogen, and no CO_2 will be formed. If the gas is carbon monoxide, the equation is



so that the contraction will be half, and the CO_2 will be equal to, the volume of gas present. Whatever the combustible gas or vapour may be, the relation between volume of gas present, contraction on combustion, and volume of CO_2 formed, must be kept in mind; and if the

relation between contraction and CO_2 formed does not correspond within the limits of error, some other combustible gas must be present.

If more than one combustible gas is present, it is generally known what these gases are, or may be; and if only two or three can be present, the percentage of each may be determined by means of the apparatus just described. If the possible gases are carbon monoxide and hydrogen (water-gas and various kinds of "producer" gas) it is clear that the carbon monoxide is equal in volume to the carbon dioxide formed on combustion. From this the contraction due to carbon monoxide can be calculated. The rest of the contraction is due to hydrogen, and will be $1\frac{1}{2}$ times the volume of the hydrogen. If the gases are methane and hydrogen (gases produced in the intestine, by cellulose fermentations outside the body, etc.), a corresponding mode of calculation is applicable.

If only two gases are present, but they both contain carbon, their proportions can still be calculated from the contraction and CO_2 formed. Let us suppose that the two gases are methane and carbon monoxide. As already explained, one volume of methane gives two volumes of contraction and one volume of CO_2 , while one volume of carbon monoxide gives half a volume of contraction and one volume of CO_2 . Hence if the symbols CH_4 and CO represent the percentages present of each of these gases, we have the following equations:—

$$(1) 2\text{CH}_4 + \frac{1}{2}\text{CO} = \text{percentage contraction.}$$

$$(2) \text{CH}_4 + \text{CO} = \text{percentage of } \text{CO}_2 \text{ formed.}$$

By multiplying both sides of the second equation by two, and subtracting equation (1) from the product, we find that $1\frac{1}{2}$ CO = twice the percentage of CO₂ formed, minus the percentage contraction. From this result, and equation (2), it is easy to calculate the percentages of CO and CH₄, and also the percentage of oxygen consumed in their combustion.

In most ordinary cases where such gases as methane and carbon monoxide occur together hydrogen is also present, or may be present; and in many cases where hydrogen and carbon monoxide are present methane may also be present. This is the case, for instance, in mine air vitiated by the after-damp of an explosion of coal-dust or methane, gases from explosives, or from coal which has heated, etc., also in exhaust gases from internal combustion engines, flue-gases, etc., where the combustion has been imperfect. In such cases it is necessary to determine not only the contraction and CO₂ formed, but also the oxygen consumed. For this purpose it is necessary to make two analyses: the first to determine the carbon dioxide, contraction on combustion, CO₂ formed on combustion, and residual oxygen; and the second to determine the oxygen originally present in the sample.

The following is an example of an analysis of a sample of air vitiated by the products of explosion of gelignite, and also to some extent by products of respiration, etc. The sample was taken in a "rise" in a metalliferous mine five minutes after eight bore-holes had been blasted.

First Analysis.

Volume of air taken	.	.	20.298	
After CO ₂ absorbed.	.	.	19.740	
			<hr/>	
∴ CO ₂		=	0.558	= 2.75 per cent.
After combustion ¹	.	.	19.707	
			<hr/>	
∴ contraction		=	0.033	= 0.165 per cent.
After CO ₂ absorbed.	.	.	19.659	
			<hr/>	
∴ CO ₂ formed		=	0.048	= 0.24 per cent.
After residual oxygen absorbed			15.668	
			<hr/>	
∴ residual oxygen		=	<u>3.991</u>	= 19.66 per cent.

Second Analysis.

Volume of air taken	.	.	20.294	
After CO ₂ absorbed.	.	.	19.736	
			<hr/>	
∴ CO ₂		=	0.558	= 2.75 per cent.
After O ₂ absorbed	.	.	15.719	
			<hr/>	
∴ O ₂		=	<u>4.017</u>	= 19.795 per cent.

From the two oxygen determinations it follows that the oxygen consumed in the combustion of the gas in the sample was $19.795 - 19.66 = 0.135$ per cent. The contraction on combustion was 0.165 per cent., and the CO₂ formed 0.24 per cent.

In the explosion of gelnite and combustion of the

¹ To simplify the statement, the very slight differences observed on a second combustion are not separately set down.

fuses the only gases formed in appreciable quantities are CO, H₂, and traces of CH₄. The proportions in which these gases produce contraction on combustion and formation of CO₂ have already been stated, and CO and H₂ each consume half their volume of oxygen, while CH₄ consumes twice its volume of oxygen. Hence if, as before, the symbols CO, H₂, and CH₄ are taken to represent the percentages present of each of these gases, we have the following equations:—

$$\begin{aligned} (1) \text{ CO} + \text{CH}_4 &= 0.24 \text{ per cent.} \\ (2) \frac{1}{2}\text{CO} + 2\text{CH}_4 + 1\frac{1}{2}\text{H}_2 &= 0.165 \text{ per cent.} \\ (3) \frac{1}{2}\text{CO} + 2\text{CH}_4 + \frac{1}{2}\text{H}_2 &= 0.135 \text{ per cent.} \end{aligned}$$

By subtracting (3) from (2) we find that H₂=0.03 per cent.; and from (1) and (2), after eliminating H₂ from (2), we find that CH₄=0.00 and CO=0.24.

The result of the analysis is therefore as follows:—

Oxygen	19.795
Carbon dioxide	2.75
Carbon monoxide	0.24
Hydrogen	0.03
Methane.	0.00
Nitrogen	77.185
	<hr/>
	100.00
	<hr/>

When more than three gases or vapours are present they cannot be separately determined by the apparatus described above. For instance, in the complete analysis of lighting gas, which contains hydrogen, methane, ethane, carbon monoxide, ethylene, benzene, etc., much more com-

plicated procedures are needed. For some purposes, however, as in determining the percentage of lighting gas in a mixture of the gas with air, it is quite sufficient to determine the contraction or the CO_2 formed on combustion, provided that it is known what contraction, or formation of CO_2 , a given volume of the original gas gives.

Management of Apparatus.—After an analysis the taps should be so turned as to disconnect the burette from the absorption pipettes and open the control tube to the air. Unless this is done a fall of temperature or rise of barometric pressure may cause the potash to be sucked over.

At the end of an analysis the nitrogen left over should be kept. It should be stored in the pyrogallate pipette if, in the next analysis, a determination of oxygen is not needed. It can then be used to wash out the connections before any future determination of oxygen.

If through any accident potash or pyrogallate solution has been sucked over, the taps are sure to stick unless they are carefully cleaned. The burette must, of course, also be cleaned out. For this purpose any potash solution should first be driven out of the burette. Water acidified with a little sulphuric acid is then introduced from a pipette the end of which is pushed into the rubber tubing on the free limb of the three-way tap at the top of the burette. The dilute acid is allowed to run down to the bottom of the burette, and is then cautiously passed along the connecting tubes and down to the marks in the absorption pipettes, so as to remove all alkali. After this operation is complete the acid is driven out of the burette again as completely as possible,

but, of course, leaving the glass moist. The taps are then all removed, wiped clean, together with their seatings, and greased with a fresh layer of vaseline. Should a tap jam it should be heated cautiously with a Bunsen flame, which will usually loosen it; but it may have to be cut out, and a fresh one substituted.

The burette should be cleaned with nitric acid whenever it begins to look dirty. For this purpose the rubber tubing connecting it with the mercury reservoir is detached, and nitric acid from a small porcelain capsule sucked up cautiously with the help of rubber tubing attached to the free limb of the three-way tap. The nitric acid is afterwards washed out thoroughly with water, and finally with very dilute sulphuric acid.

If the joints in the connecting tubing to the absorption pipettes have been made with soft and thick red rubber tubing they should be perfectly tight from the beginning, and should remain tight. They do not need wiring. The tap should also be tight. A tap that is so badly ground as to leak occasionally should be changed. To test for leakages, heavy pressure should be brought on the different joints in succession. To do this the tap at P should first be turned so as to shut off connection with the control tube or outer air. The connecting tube between the potash pipette and R is then compressed firmly with one hand and squeezed with the other at a point nearer the potash pipette. By this means the pressure in the potash pipette is greatly increased, and any leakage between the potash pipette and the burette is revealed by the potash creeping up from the mark M.

The connections of the combustion and pyrogallate pipettes and control tube are all tested by similar methods, and there is no difficulty in rapidly detecting any leakage. The powder used for dusting the inside of the rubber tubing may cause slight and very troublesome leaks. These do not occur if the rubber is perfectly clean and smooth, or if a little vaseline is used.

A possible source of slight error in the carbon dioxide determinations is the fact that when the potash pipette is first charged the potash may dissolve a little sulphide from sulphur present in the rubber. The potassium sulphide may then absorb an appreciable quantity of oxygen when air is passed into the pipette, so that in successive blank experiments with air the reading is slightly lower each time. If the potash has begun to turn yellow some sulphide is sure to be present, and the pipette should be recharged with fresh solution. If, however, black rubber tubing is used for connecting the potash pipette with the potash reservoir, this source of error can easily be avoided. In the earlier forms of the apparatus the potash pipette was closed below by a red rubber cork, which continued for long to give off sulphide.

To test the efficient working of the apparatus it is an excellent plan to make an analysis of outside air. After the carbon dioxide has been absorbed the reading of the burette should be the same after repeated passage of the air into the potash pipette, or into the combustion pipette, whether or not the spiral has been heated. After the oxygen has been absorbed the reading should also remain steady after repeated passing of the air into

the pyrogallate pipette; and the percentage of oxygen, or at any rate the sum of the percentages of carbon dioxide and oxygen, should be the same for each analysis. If any leakage or other source of accidental error exists anywhere it will be detected by these tests. They are quite indispensable for a beginner, and will soon give him an idea of the great accuracy attainable in gas analysis, and of the degree in which he has mastered the technique of properly adjusting the levels, reading the mercury meniscus, etc. If everything is right the errors of reading and adjusting the pressure ought not to exceed $\cdot 001$ c.c., corresponding to $\cdot 005$ per cent. of the volume read off.

Testing the Burette.—It seldom, if ever, happens that a gas-burette is graduated correctly all the way down to $\cdot 001$ c.c.; and often the error is sufficient to make a very appreciable difference in the results, particularly as regards the oxygen percentage. Unless these errors are corrected, wrong deductions may be drawn, and different analyses are not comparable exactly with one another. As already explained, a burette may be checked by weighing with mercury; but this method has the disadvantage that the burette has to be inverted unless a tap is fused on at the lower end, so that an error arises on account of the mercury meniscus facing what ought to be the lower end of the burette. This error can only be roughly allowed for. It is also desirable to be able to check the graduation at any time, and under the exact conditions under which it is being used. There is fortunately a very ready and easy

means of doing this. In pure outside air Nature has furnished us with a gas-mixture of practically constant composition, so that by an analysis of such air we can check the graduations of a burette.

With a gas-burette of which the graduation has been very carefully checked in duplicate in the upright position (a glass tap having been fused on below for the purpose), and with moisture inside the burette just as in an actual analysis, the writer found that the composition of pure outside air was as follows:—

Oxygen	20·93
Carbon dioxide	0·03
Nitrogen (including argon)	79·04
	<hr/>
	100·00
	<hr/>

It does not seem probable that there is any variation from these figures by more than ·005 per cent. By the gravimetric method (described below) the carbon dioxide percentage can be determined easily to the third place of decimals or further, and by this method it can be shown that in summer weather—in consequence of carbon dioxide being absorbed by green plants during the day, and being given off from plants and from the the ground during the night—the percentage of carbon dioxide in the lower strata of air may vary from about ·025 to ·035. The oxygen doubtless varies correspondingly in the opposite direction, though this has never yet been demonstrated; but a variation of ·005 per cent. is within the error of experiment with the

apparatus just described. The writer has never observed with this apparatus any sensible variation in the oxygen percentage in the air at Oxford or elsewhere at different times. In large towns the carbon dioxide may rise quite appreciably in the outside air, especially during winter, and it is common to find $\cdot 04$ or $\cdot 05$ per cent. of carbon dioxide. During a dense black fog as much as $\cdot 14$ per cent. was found by Russell in outside air in London. As the excess of carbon dioxide in the air of a large town is due mainly to combustion of coal, the excess of carbon dioxide will be accompanied by a slightly greater deficiency of oxygen. Except in very foggy weather, however, we may assume that the sum of oxygen and carbon dioxide remains the same in all outside air, even in a town. This sum amounts to $20\cdot 96$ per cent.; so that if a burette is graduated correctly the oxygen and carbon dioxide of outside air should together give $20\cdot 96$ per cent.

The following four successive analyses of the same sample of outside air, with the corrected burette just referred to, will give an idea of the limits of accuracy attainable with the apparatus described above.

	Oxygen.	Carbon Dioxide.
No. 1	20·930	·025
„ 2	20·926	·030
„ 3	20·931	·035
„ 4	20·924	·030
Mean	20·928	·030

If it is found that a burette gives 21.06 for the sum of the oxygen and carbon dioxide the error is 0.1 in 21.06, or almost exactly $\frac{1}{210.6}$ of the percentage of oxygen, so that the percentages obtained should always be corrected by deducting $\frac{1}{210.6}$. If the burette has been skilfully graduated, this error is almost certain to be due to error in measuring the volume from the top of the graduation to the tap; and the error usually met with in a burette is caused by this space being under-estimated, owing to the mercury meniscus having been read off with the burette inverted for the purpose of graduation.¹ An error of this kind is easily corrected by deducting $\frac{1}{210.6}$ from the percentage of each gas as estimated with the burette. Thus, if the carbon dioxide were given by the burette as 6.06 the corrected result would be 6.03 (provided that the burette had been completely filled with the sample to be analysed).

Errors in a burette might, however, arise from mistakes in the graduation of the graduated part of the burette; and if so this simple method of correction would not be applicable. To test the graduation in the graduated part the following method can be used. The burette is filled with air to near the bottom of the graduations and carefully read off, with the usual precautions. About 1 c.c. is then shunted into the explosion pipette (which had previously been adjusted accurately to the mark), and the burette again read off, so that the volume of air shunted is accurately known.

¹ Burettes graduated in the upright position, with a tap fused on below, are now supplied by Siebe, Gorman & Co.

About 1 c.c. is then expelled to the outside, and the burette again read. The measured volume of air is then returned from the explosion pipette, and another reading made. If the graduation is even, the volume of air returned should read exactly the same as it did when read off on the lower part of the burette. By repeating this process right up the graduated part the whole of the graduations can be tested, and they should show no sensible irregularity. A burette with uneven graduation of the stem should be rejected.

It is evident that when it has been necessary to dilute the sample taken in with 15 c.c. or more of nitrogen or air, as in certain of the examples quoted above, there will be no correction to be made in the percentages found, provided that the graduation of the stem of the burette is even.

If a burette is allowed to get dirty inside, it will be found that the oxygen determinations with it come out very appreciably higher than when it is clean. The difference may amount to as much as 10 per cent. if the burette is very dirty. It is therefore desirable to clean the burette pretty frequently, or, failing this, to control the error by occasional analyses of outside air.

Plain Burette for measuring Gas.—In certain cases it is necessary not only to analyse a sample of gas, but also to measure its volume. For instance, the gas exhausted from a given volume of blood or other liquids by the mercury pump has to be measured as well as analysed. For this purpose the form of burette described above will not answer, and a plain straight burette is

needed. Fig. 9 shows such a burette, with its water-jacket, control tube, and levelling-tube. It is connected with the absorption and combustion pipettes in exactly the same way as the burette described above, and the method of using it for an analysis is exactly the same, though the accuracy attainable is, of course, not so great. The gas is collected in the collecting tube shown in fig. 4, and the whole of it is transferred to the burette in the ordinary way. The control tube is opened just before the analysis, so that the gas is measured at the existing atmospheric pressure, which is read off on the barometer. The temperature in the jacket is also read off. The volume of the gas, dry, and at standard pressure and temperature, can then be calculated in the ordinary way, or more conveniently from the table on p. 60.

Description of Smaller Apparatus. —

The apparatus described above occupies permanently a good deal of space, and cannot easily be moved about. For this reason a smaller and easily portable apparatus on exactly the same principle was afterward designed by the writer, and has proved extremely useful, both for laboratory work and for use at any other place where it was required. It was originally designed for use on



FIG. 9. — Plain Burette for both Measuring and Analysing Gas.

shipboard during an investigation of physiological conditions in deep diving,¹ and it has proved very convenient in physiological experiments out of doors, on high mountains, etc.: also in experiments underground in mines.

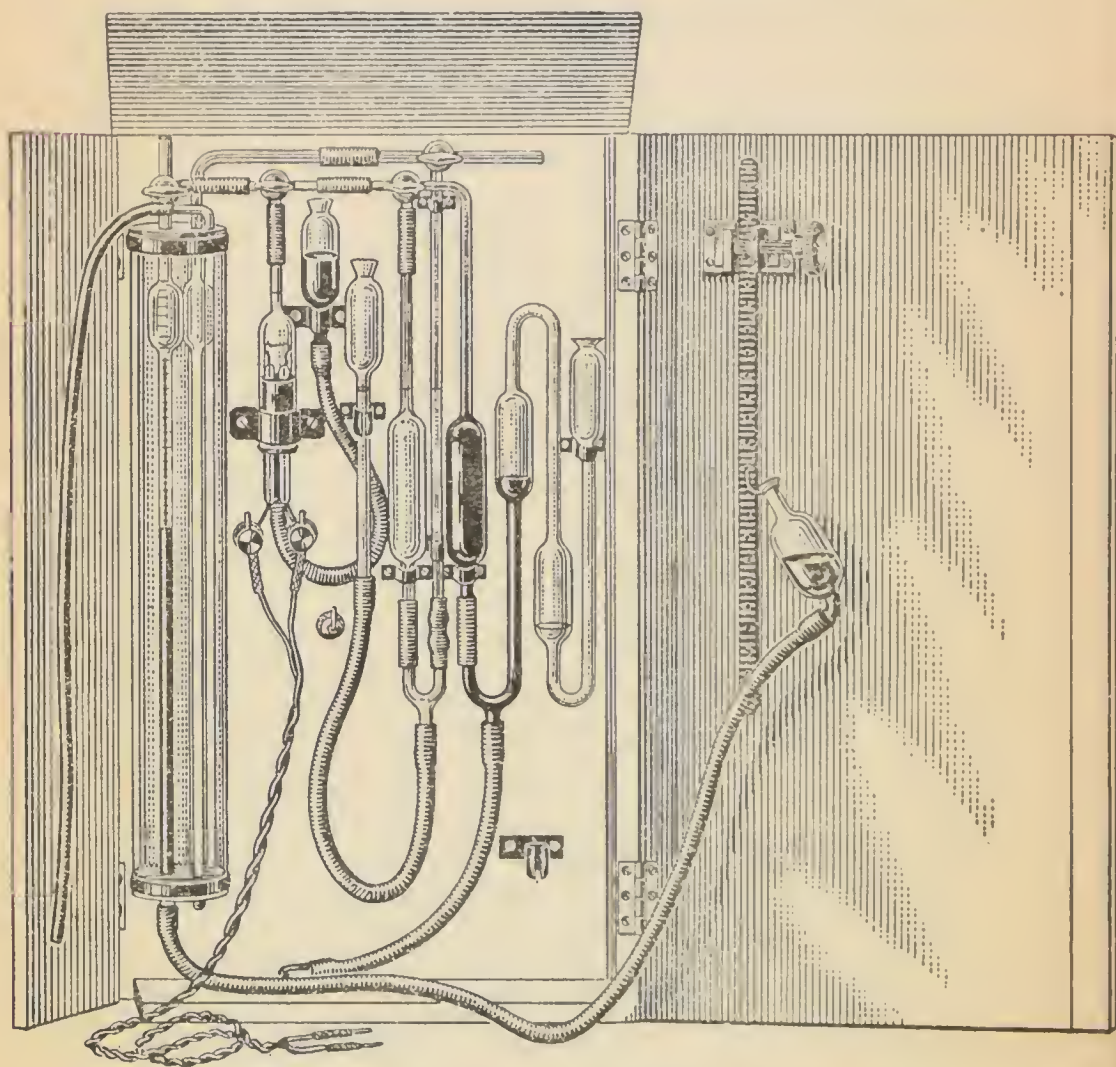


FIG. 10.—Smaller Apparatus for General Air Analysis.

The apparatus is shown in fig. 10. It is contained in a wooden case, of which the internal measurements are

¹ *Report of the Admiralty Committee on Deep Diving*, Parliamentary Paper [C.N. 1549], 1907.

$20 \times 12 \times 2\frac{1}{2}$ inches. This can easily be shut up and transported from place to place without disturbing the absorbent solutions, etc., so that the apparatus is always ready for use. It is well, however, to cork up the open tops of the mercury and potash reservoirs when the apparatus has to travel, as it might fall over or be laid flat in ignorance. The front, top, and one side are hinged. There must be a clearance of at least an inch between the lower end of the burette and the bottom of the case.

The principle adopted and the method of use are exactly the same as in the larger apparatus, so a detailed description is unnecessary. The only points of difference, apart from the arrangement in a case, are as follows: (1) The capacity of the burette is 10 c.c., instead of 21 c.c., the absorption and combustion pipettes being correspondingly reduced in size, and the weight of mercury, water, etc., thus reduced to within easily manageable proportions. (2) The graduated portion of the burette contains only 3 c.c. instead of 6 c.c., and is thus half the length, though of the same diameter. (3) The arrangement of the combustion and absorption pipettes is slightly different, as shown in the figure. (4) In place of the levelling-tube there is a mercury reservoir. When not in use this is held by the spring clamp close to the bottom of the case, and the rubber tubing connecting the reservoir and burette is kept out of the way by hooking it over a hook, which is shown in the figure, just below the sliding potash reservoir. The case can then be shut up without difficulty. During use the reservoir

is hooked into one or other of several holes shown on the rack of the rack and pinion fixed on the door of the case. By raising or lowering the rack the level can be adjusted very exactly. (5) The wires carrying current to the platinum spiral are connected to two binding screws on the back of the case, so that the wires from the rheostat and source of current can be connected with these binding screws. This is a safer arrangement than connecting them directly.

If the apparatus is being used on ship-board, and the vessel is not quite steady, it is necessary to place two screw clamps on the rubber tubing connecting the reservoir with the burette. When the level has been roughly adjusted, the clamp farthest from the burette is screwed home: the level can then be adjusted exactly by gradually screwing up or loosening the other clamp. In using the apparatus in mines, etc., it may be supported on an ordinary artist's easel, with pegs long enough to support the case securely. Of course the case is not vertical, but this does not matter.

With care in using the apparatus the limit of error is about .01 per cent, so that successive analyses of the same sample should not differ by more than .02 per cent. The apparatus should be tested, and the graduation checked, by means of air analyses, as with the larger apparatus. Unless the burette is graduated in the upright position the error of the maker in estimating the volume of the bulb of the burette is apt to be proportionally larger than in the case of the larger apparatus, since

the absolute error will be about the same, while the volume of the bulb is only half as great. An error of one-hundredth in the percentages given by the apparatus may thus have to be corrected for, although in other ways the graduation may be perfect.

The graduation may be tested with the burette in its ordinary position, and with moisture inside, by the following method, devised by Dr C. G. Douglas. A glass tap, with narrow glass tubing, is attached by a joint of stout rubber tubing to the lower end of the burette. The glass tubing dips into a vessel of mercury. Mercury is sucked up from this vessel to the lower level of the graduations by applying suction through the tap at the upper end of the burette. Both this tap and the tap joined on below are then closed, the vessel of mercury weighed, and the burette carefully read off. Mercury is then again sucked up about 1 c.c. further, the weighing and reading off repeated, and so on up to the top of the burette. The weight of mercury sucked in each time can then be compared with the readings of the burette, due allowance being made for temperature, which is observed in the water of the jacket. By this method the pressure on the rubber joint remains constant, so that there is no error due to the joint giving, and it is unnecessary to fuse on a tap below or otherwise disturb the apparatus. The same method can be applied to the other forms of burette described below, but of course not to the long burette, which is over 30 inches in length.

The following examples, in which the procedure was

the same as with the larger apparatus, will suffice to illustrate the use of the apparatus.

1. *Determination of the Percentage of Coal-gas in the Air of an Experimental Chamber.*

(A) Partial analysis of undiluted coal-gas:—

Air taken 8.540

+ undiluted coal-gas . . . 9.486

\therefore coal-gas taken = 0.946

After combustion 8.020

\therefore contraction = 1.466

\therefore ratio of gas taken to contraction = $\frac{1.466}{0.946}$.

(B) Partial analysis of the air in the chamber:—

Air taken 9.996

After combustion 9.822

0.174 = 1.74 per cent.

\therefore coal-gas present = $1.74 \times \frac{.946}{1.466} = 1.12$ per cent.

2. *Analysis of Alveolar Air from the Lungs.*

Volume taken 9.588

After CO₂ absorbed . . . 9.050

\therefore CO₂ = 0.538 = 5.61 per cent. = 5.58 per cent. corrected.

After O₂ absorbed . . . 7.692

\therefore O₂ = 1.358 = 14.16 per cent. = 14.09 per cent. corrected.

The following results of consecutive uncorrected analyses of outside air illustrate the degree of accuracy attainable, and the correction of the burette.

	CO ₂ .	O ₂ .
	0.04	21.04
	0.02	21.03
	0.03	21.04
Mean	<u>0.03</u>	<u>21.037</u>

As atmospheric air contains 20.93 per cent. of oxygen the error in the percentages given by this burette was $\frac{1}{20.93}$, and the results must be corrected by this amount, as shown in analysis (2). As the graduation of the stem was even, there was no correction needed in analysis (1) A, and in (1) B the correction fell within the error of experiment.

Special Apparatus for Carbon Monoxide.—Several methods have been employed for the direct estimation of carbon monoxide by means of heated iodine pentoxide. The reaction which occurs is $5\text{CO} + \text{I}_2\text{O}_5 = \text{I}_2 + 5\text{CO}_2$. Graham and Winmill¹ have recently described a method by which this reaction is used in connection with the larger type of air analysis apparatus described above, so that the determinations can be carried out very accurately with the usual small samples of air.

The ordinary absorption pipettes of the large apparatus are replaced by three caustic potash pipettes, a bromine pipette, and a U-tube containing about 2 grammes of

¹ *Trans. of the Chemical Society*, 1914, vol. cv. p. 1996.

iodine pentoxide and immersed in a water-bath, as shown in fig. 10A.

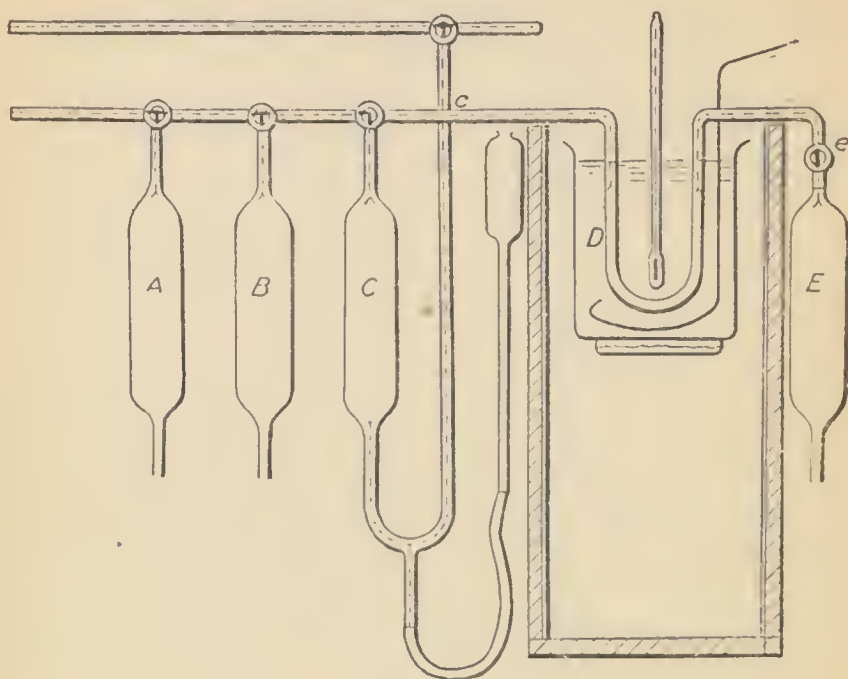


FIG. 10A.

“A contains 25 per cent. potassium hydroxide solution, C and E, 45 per cent. potassium hydroxide solution, B, bromine in an aqueous solution of potassium bromide, and D is a small U-tube so filled with powdered iodine pentoxide that the ‘dead space’ in the tube is reduced to a minimum.

“The potassium hydroxide and bromine pipettes are connected to suitable reservoirs. The pipette C is connected through a T-piece to the usual compensating device employed on the Haldane apparatus. After filling with pure iodine pentoxide, the U-tube is heated to 200° for three or four hours in a current of dry air before being fitted to the apparatus. A broad wooden

shield on either side protects the various pipettes from absorbing heat while the iodine pentoxide tube is being heated. The sample for analysis is taken into the burette and measured (1) with the usual precautions adopted when using the Haldane apparatus, the U-tube of iodine pentoxide being immersed in a bath of cold water, the temperature of which is noted. The sample is then passed into the bromine pipette, B, where it is kept for four minutes, the burette tap and those leading to A and C being closed. By opening the necessary taps and lowering the reservoir attached to C the sample is then transferred to the pipette C. The tap to B having been closed to the bromine pipette, the sample is passed several times backwards and forwards between C and A to remove all bromine vapour, and is then brought back into the burette and measured. The operation is repeated until a constant reading (2) is obtained. The difference between (1) and (2) gives the amount of carbon dioxide, hydrogen sulphide, sulphur dioxide, and unsaturated hydrocarbons. The latter are completely removed by two passages into the bromine pipette provided the amount does not exceed 5 per cent., the second passage only being necessary to wash out the 'dead space' between the burette and the bromine pipette. The sample is next passed into the pipette C and the tap on this pipette opened to the U-tube, which is now heated to 90–100°, the beaker of cold water being replaced by one containing hot water and heated by means of a small Bunsen burner during the oxidation of the carbon monoxide. The sample is passed from C to

E through the iodine pentoxide U-tube, D, twice backwards and forwards by raising or lowering the reservoir attached to C. By this means the carbon monoxide is oxidised to the dioxide, which, together with the iodine liberated, is absorbed by the alkali in C and E. The residual gas in the connexions between the burette, A, B, and C, is 'washed out,' and the gas sample again passed backwards and forwards twice over the hot iodine pentoxide. This has been found sufficient to remove completely all the carbon monoxide even when 15 per cent. is present in the original sample. (The complete removal of carbon monoxide has been demonstrated by constancy of volume after subjection to further passages over the hot iodine pentoxide, and also by the delicate 'blood' test.) The beaker of hot water is then removed and replaced by the original beaker of cold water, and after a couple of minutes the potash level in E is brought to the graduation mark, the temperature of the water-bath being again noted. In cases where there is any small variation in temperature, a correction, readily determined by experiment, is applied. This correction should not exceed 0.002 c.c. per 1° change in temperature in a well-constructed iodine pentoxide tube. The sample is transferred to the burette and measured (3), the difference between (2) and (3) giving the amount of carbon monoxide present.

"It will be noticed that the gas sample is confined over 45 per cent. potassium hydroxide solution during the oxidation, and is therefore not quite dry. Previous investigators have insisted that the sample must be free

from moisture for complete oxidation of the carbon monoxide, but this is apparently unnecessary, although we have found it advisable to heat the iodine pentoxide to about 190° in a current of dry air after about twenty analyses. This is probably due to the fact that moisture has been present in the gas sample passed over the iodine pentoxide. For simplicity in manipulation the U-tube is connected to the apparatus by means of rubber junctions at *c* and *e*, no objection having been found to the adoption of this plan."

As unsaturated hydrocarbons act upon iodine pentoxide, it is necessary to remove them by means of the bromine pipette; and the iodine or bromine must not be allowed to pass into the burette, as the mercury would be contaminated. It was found that though methane is never acted on by the iodine pentoxide, hydrogen is oxidised to a sensible extent if more than 20 per cent. of hydrogen or 8 per cent. of CO is present. Hence if the sample contains more than 20 per cent. of hydrogen, or more than 8 per cent. of CO, it should be diluted with air. This can easily be done in the burette in the manner already described. Thus the method can be very conveniently used for the direct determination of carbon monoxide in coal-gas, as well as for carbon monoxide in products of combustion or explosion.

The following analyses show that the limit of error is about 0.02 per cent.:—

A. Mixtures of Carbon Monoxide with Air.

Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.	Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.
0.02	0.02	3.06	3.09
0.08	0.10	3.43	3.41
0.11	0.11	8.21	8.20
0.11	0.10	10.22	10.21
0.22	0.22	16.12	16.13
0.39	0.38	24.13	24.14
1.50	1.51		

B. Mixtures containing less than 20 per cent. of Hydrogen and less than 8 per cent. of Carbon Monoxide.

Hydrogen present, per cent.	Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.
6.38	5.47	5.47
8.30	8.44	8.44
14.00	7.39	7.38
14.00	7.45	7.43
18.80	7.87	7.88
19.58	5.66	5.68

C. Mixtures of Natural Fire-damp with Carbon Monoxide and Air.

Fire-damp present, per cent.	Carbon Monoxide added, per cent.	Carbon Monoxide found, per cent.
10.85	0.00	0.00
79.00	0.00	0.00
79.00	0.00	-0.01
10.8	0.18	0.19
10.7	1.12	1.15
74.6	1.98	2.01
70.6	2.60	2.59

CALCULATION AND STATEMENT OF RESULTS OF ANALYSES.

WHEN numerous analyses have to be calculated out from readings of the burette, and subsequent calculations probably made, as in physiological work, or work on mine air, it saves a good deal of time to use a slide-rule. The ordinary ten-inch slide-rule is not accurate enough, however, for exact work ; and a slide-rule which permits of working accurately to five figures is needed. A Fuller's spiral slide-rule¹ will be found very convenient.

In some cases nothing more is needed than the bare percentages of the gases present ; but often further calculations are required.

Physiological Analyses.—We may first take the case of physiological analyses of respired air. What has been analysed is usually a sample of a large volume which has been measured by an experimental gas-meter, or is contained in a space of known volume ; and it is required to calculate the volume at 0° C. and 760 mm. pressure of the carbon dioxide which has been given off into this volume of air and the oxygen which has been absorbed from it : also the “respiratory quotient”

¹ Made by Stanley & Co., Great Turnstile, Holborn, London.

or ratio by volume of carbon dioxide given off to oxygen absorbed.

The first step is to reduce the volume of the air which has been measured to its volume when measured dry at 0° C. and 760 mm. barometric pressure. This process is so frequent in work involving air analysis that it saves much trouble to calculate to three figures from the accompanying table, showing for ordinary barometric pressures and indoor temperatures the volume to which 100 volumes of air are reduced. The volume has practically always been measured with the air saturated with moisture, which simplifies the table.

TABLE FOR REDUCTION TO DRY AIR AT 0° C. AND 760 MM. OF 100 VOLUMES OF AIR SATURATED WITH MOISTURE AT DIFFERENT TEMPERATURES AND PRESSURES.

Temperature °C.	Barometric Pressure in Inches or Millimetres.								
	29.13 740	29.33 745	29.53 750	29.72 755	29.92 760	30.12 765	30.31 770	30.51 775	30.71 780
10	92.77	93.39	94.04	94.66	95.30	95.93	96.57	97.21	97.84
11	92.36	92.98	93.63	94.25	94.89	95.52	96.16	96.79	97.42
12	91.95	92.55	93.18	93.80	94.44	95.07	95.70	96.33	96.96
13	91.54	92.17	92.80	93.41	94.05	94.68	95.31	95.94	96.57
14	91.13	91.76	92.38	93.00	93.62	94.26	94.88	95.51	96.13
15	90.71	91.34	91.96	92.57	93.20	93.82	94.44	95.08	95.70
16	90.29	90.92	91.54	92.15	92.78	93.40	94.01	94.64	95.26
17	89.87	90.50	91.11	91.72	92.35	92.97	93.58	94.21	94.83
18	89.45	90.08	90.68	91.30	91.92	92.54	93.15	93.77	94.39
19	89.02	89.64	90.25	90.86	91.48	92.09	92.71	93.32	93.94
20	88.59	89.21	89.81	90.41	91.04	91.65	92.26	92.88	93.50
21	88.18	88.86	89.40	90.01	90.62	91.23	91.84	92.45	93.07
22	87.71	88.32	88.90	89.53	90.14	90.75	91.36	91.97	92.60
23	87.26	87.87	88.47	89.08	89.69	90.29	90.90	91.51	92.13
24	86.81	87.43	88.01	88.62	89.23	89.83	90.44	91.04	91.65
25	86.35	86.96	87.57	88.17	88.79	89.38	89.98	90.57	91.17

Let us suppose, for instance, that the volume of air expired in exactly ten minutes was 70.4 litres, and that the temperature of the gas-meter was 18.5° , and the barometric pressure 748 millimetres. From the table the factor for correction is evidently about .902, and the reduced volume is therefore $70.4 \times .902 = 63.5$ litres.

Let us now suppose that the inspired air was pure, and contained 20.93 per cent. of oxygen, 0.03 of carbon dioxide, and 79.04 of nitrogen; and that the sample of the expired air contained 16.41 per cent. of oxygen, 3.62 of carbon dioxide, and 79.97 of nitrogen. It is clear that the volume (at 0° and 760 mm., dry) of carbon dioxide given off was $\frac{3.62 - .03}{100} \times 63.5 = 2.280$ litres.

The volume of oxygen absorbed is less easy to calculate, however, as the volume of dry air has diminished in the process of respiration, because more oxygen has been taken up than carbon dioxide has been given off. Since nitrogen is neither taken up nor given off in respiration it is evident that for every 100 volumes of expired air there corresponded in the inspired air, not 20.93 volumes

of oxygen, but $20.93 \times \frac{79.97}{79.04} = 21.18$ volumes. Hence the

oxygen which disappeared was $\frac{21.18 - 16.41}{100} \times 63.5 = 3.029$

litres; and the respiratory quotient was $\frac{2.280}{3.029} = 0.753$.

Had the respiratory quotient been incorrectly taken as the ratio between excess of carbon dioxide percentage

and deficiency of oxygen, *i.e.* as $\frac{3.62 - .03}{20.93 - 16.41} = .794$,

and the oxygen absorption also been calculated in a similar way, the error would have been considerable, and wrong conclusions might have been drawn as to the material being oxidised in the body, the production of heat, etc.

The following table shows the relation between the apparent respiratory quotient (*i.e.* the ratio of excess in carbon dioxide percentage to deficiency in oxygen) and the real one. With the help of the "difference" column in this table the true respiratory quotient can

TABLE FOR CALCULATING TRUE FROM APPARENT RESPIRATORY
OR COMBUSTION QUOTIENT.

Apparent Respiratory or Combustion Quotient.	True Respiratory or Combustion Quotient.	Difference.
2.00	2.72	+ .72
1.90	2.49	+ .59
1.80	2.29	+ .49
1.70	2.09	+ .39
1.60	1.90	+ .30
1.50	1.73	+ .23
1.40	1.57	+ .17
1.30	1.431	+ .113
1.20	1.266	+ .066
1.10	1.131	+ .021
1.00	1.000	± .000
.95	.937	- .013
.90	.877	- .023
.85	.817	- .033
.80	.760	- .040
.75	.704	- .046
.70	.649	- .051
.60	.543	- .057
.50	.441	- .059
.40	.345	- .055
.30	.253	- .047
.20	.165	- .035
.10	.081	- .019
.00	.000	± .000

easily be deduced for any value of the apparent one; and by dividing the output of carbon dioxide by the true respiratory quotient the intake of oxygen is at once obtained. Under normal conditions the respiratory quotient lies between 0·7 and 1; but under unusual conditions it may temporarily rise or fall much beyond these limits; and the table is extended accordingly, particularly as it is also of use in connection with analyses of mine air, exhaust gases from internal combustion engines, etc.

Analyses of Mine Air.—A complete analysis of mine air should always, of course, be stated in terms of the actual chemical constituents found. It is, however, of advantage to state the results in another form also. In nearly every case a greater or less amount of air is present in the mixture analysed. As atmospheric air is the only source of oxygen in a mine it is clear that the percentage of air in the sample can be calculated from the oxygen percentage by multiplying by $\frac{100}{20\cdot93}$. The residue left after deducting the oxygen, nitrogen, and carbon dioxide of the air, consists of nitrogen, carbon dioxide, and possibly methane, carbon monoxide, etc. The methane and any other combustible constituent ought evidently to be stated separately, so that what is left over consists of nitrogen and carbon dioxide. Now, it will be found that in the great majority of cases the composition of this residue corresponds more or less closely to that of the “black-damp” met with in unventilated parts of the mine from which the

sample comes. Hence the residue may be set down in the analysis as "black-damp."

By "black-damp" a miner practically understands any sort of gas or air which will extinguish a lamp without at the same time being capable of causing an explosion, and which will not cause symptoms of poisoning or asphyxiation when mixed with just sufficient air to allow a candle to burn. Pure black-damp, free from air, is still very commonly confused with carbon dioxide, but is really a mixture of nitrogen with a relatively small proportion of carbon dioxide. It is simply the gaseous residue resulting from the slow oxidising action of air on oxidisable substances in a mine. Hence it consists chiefly of nitrogen; and a mixture of black-damp with air has very different physical and physiological properties from a mixture of carbon dioxide with air.

The following examples illustrate the mode of statement of an analysis in terms of air, black-damp, etc., and at the same time indicate the justification for this mode of statement.

1. *Gas issuing into a Return Air-way from Old Workings through a pipe in a brick stopping, Podmore Hall Colliery, North Staffordshire.*

Oxygen	0.72
Carbon dioxide	11.03
Methane	7.47
Nitrogen	80.78
						<hr/>
						100.00
						<hr/>

Otherwise expressed.

Air	{	Oxygen	0.72	}	3.44
		Nitrogen	2.72		
		Methane		7.47
Black-damp	{	Nitrogen	78.06	}	89.09
		Carbon dioxide	11.03		
										<hr/>
										100.00

2. Air of Main Return of same Colliery.

Oxygen	20.34
Carbon dioxide	0.305
Methane	0.65
Nitrogen	78.705
						<hr/> 100.00 <hr/>

Otherwise expressed.

Air	{	Oxygen	20.34	}	97.18
		Nitrogen	76.81		
		Carbon dioxide	0.03		
		Methane		0.65
Black-damp	{	Nitrogen	1.895	}	2.17
		Carbon dioxide	0.275		
										<hr/>
										100.00

In these analyses the percentage composition of the black-damp was:—

	No. 1.	No. 2.
Nitrogen	87.6	87.3
Carbon dioxide	12.4	12.7
		5

From the latter figures it is evident that in this mine about 12·5 per cent. of carbon dioxide appeared in the air for 20·93 per cent. of diminution in the oxygen percentage owing to oxidation. The “apparent” oxidation quotient was therefore $\frac{12\cdot5}{20\cdot93}$, or 0·60, and (from the table, p. 57) the true oxidation quotient was 0·54. If 50,000 cubic feet of air per minute were passing along the main return, the production of carbon dioxide (not corrected for temperature, etc.) in the district served by this return would be $\frac{305 - \cdot03}{100} \times 50,000 = 142$ cubic feet per minute; the consumption of oxygen $\frac{142}{\cdot54} = 263$ cubic feet; and the production of methane $\frac{\cdot65}{100} \times 50,000 = 325$ cubic feet.

The oxidation quotient in different mines, and different seams of coal, varies very greatly, according to the circumstances in each case; and unless this quotient is known for a mine, incomplete analyses (for instance, determinations of carbon dioxide alone) may be very misleading.

Analyses of Exhaust Gases.—In connection with analyses of exhaust gases from internal combustion engines, the ratio between excess of carbon dioxide and deficiency of oxygen should be calculated, particularly if only carbon dioxide and oxygen are determined. If the combustion is complete, the oxidation quotient, calculated from this ratio by the help of the table, should correspond to that calculated from the composition of the fuel; and any fall in this ratio would indicate incomplete combustion.

PORTABLE APPARATUS FOR DETERMINING SMALL PERCENTAGES OF CARBON DIOXIDE.¹

THE percentage of carbon dioxide in the air of ordinary rooms, schools, factories, etc., is a convenient index of the degree of vitiation of the air by respiration and lights. Hence the determination of the small percentages of carbon dioxide present in such air is a matter of considerable practical importance, and the apparatus now to be described was introduced for the purpose of making this determination rapid and convenient.

The apparatus is shown in fig. 11. In general principle it is similar to that already described, but with modifications designed to make the process of analysis as rapid and simple as possible. The construction and arrangement will be evident from the figure.

The air-burette A, which is enclosed in a water-jacket with glass face, consists of a wide ungraduated and a very narrow graduated portion. It holds 20 c.c. from the tap to the bottom of the scale. The graduated part, which is 4 inches long, is divided into about one hundred divisions, each of which corresponds to

¹ Described in its original form in the *Journal of Hygiene*, 1901, p. 109, and in the *First Report of the Departmental Committee on Factory Ventilation*, Parliamentary Paper [Cd. 1302], 1902.

$\frac{1}{10000}$ th part of the capacity of the burette, when moist, for mercury. The lowest division is marked 0, and the numbering is upwards from this point. Any difference

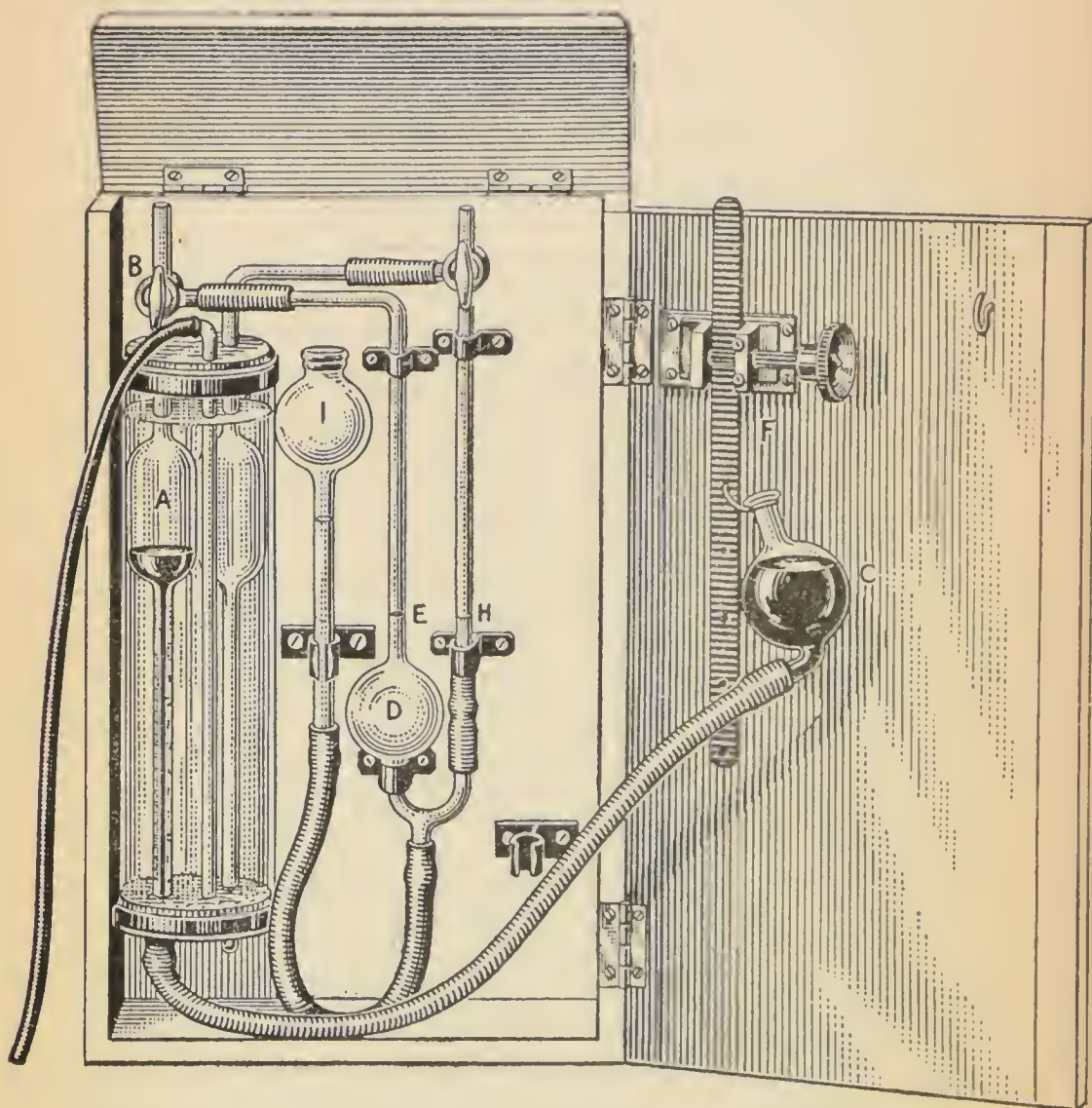


FIG. 11.—Portable Apparatus for Small Percentages of Carbon Dioxide.

between a reading at or near zero and a second reading is thus shown by the scale in volumes per 10,000, there being no calculations or corrections.

In using the apparatus the potash level is first adjusted to the mark at E. The air is then expelled from the burette by opening the three-way tap B to the outside and raising the mercury bulb C. The tap B is then closed by turning it one-eighth round, and the mercury bulb is lowered and placed on the hook of the rack-and-pinion arrangement F, which is arranged at such a level that on opening the tap to take in a sample the mercury in the burette falls to about the zero-mark. The sample is taken in at any desired part of a room by carrying the apparatus to the place. If the burette is allowed to fill while the apparatus is carried across the room, a good average sample can be obtained. As it takes some seconds for the mercury to run down, this method of taking the sample can easily be adopted.

The apparatus is now placed on a table, the water in the jacket mixed by blowing through it, the potash level in the tube H adjusted exactly to the mark by raising or lowering the reservoir I, and the three-way tap at the top of the tube H turned so as to close communication with the outside air and leave H in communication with the control tube. The potash level in E is also brought exactly to the mark by raising or lowering the mercury reservoir, and the mercury level in the burette is then read off. Before doing so it is well to mix the water in the bath again, and to pinch the rubber tube leading to the potash reservoir to make sure that the liquid in the two gauge tubes moves quite freely and returns exactly to the marks. It occasionally happens that a tap is blocked by a drop of mercury, or some vaseline, so that

the gauge does not move freely till the obstruction is broken through.

The air is now driven over into the potash pipette (which is filled with caustic potash or soda solution of about 10 per cent. strength) and back at least twice, and a second reading taken with the same precautions, after again thoroughly mixing the water in the jacket. The difference between the two readings gives the proportion of carbon dioxide in volumes per 10,000.

After the analysis the control tube is opened to the air and the burette shut off from the potash pipette. It is most important not to forget this, as potash may otherwise be sucked up, with the result that the apparatus is fouled and the taps possibly jammed.

If the samples of air are collected in bottles (fig. 1) and analysed afterwards, they are transferred to the apparatus with the help of the trough and curved tube described already (fig. 7). As, however, the sample is removed at a negative pressure there is difficulty in afterwards equalising the pressure in the very narrow burette, unless provision is made for the purpose. An extra three-way tap should therefore be attached to the tap of the burette, as shown in fig. 12. In taking in the sample the mercury reservoir is depressed below the level of the table, so that when the extra tap is closed and the mercury replaced on the hook, the pressure in the burette is positive. On opening the extra tap to the outside the excess of pressure is blown off, and the mercury comes to the zero-point, or a little

above it, after which the analysis may be proceeded with in the ordinary way.

The efficient working of the apparatus should be checked by making repeated readings with the same sample of air, first freed from CO₂. The reading should

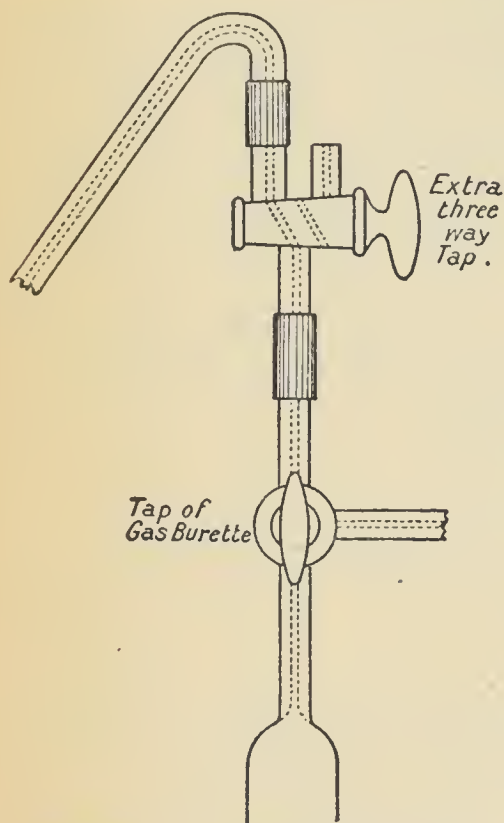


FIG. 12.—Arrangement of Extra Three-way Tap.

be the same within one division after repeatedly passing the air into the potash pipette. Any leakage would be shown by this test,¹ and the joints or taps can also be tested by putting pressure on them successively, as explained in connection with the large apparatus (p. 40). It is important to note that the burette must always be kept moist with a very small quantity of water acidified with sulphuric acid, as with the large apparatus. If the burette

is dry, a determination will probably give an apparent negative result, due to the air taking up aqueous vapour from the potash. It is also most important to keep the burette clean by occasional washing with nitric acid.

¹ This test would also reveal any absorption of oxygen by sulphide given off by the rubber tubing—an occurrence which must be guarded against in the manner explained in connection with the larger apparatus (p. 41).

Dirt in the stem of the burette may make the results very appreciably too high. If a tap jams and cannot be loosened by heating, it may be cut out and a new one fixed in position by rubber tubing.

To check the calibration of the burette, the mercury which flows out between different points can be weighed with the burette in the inverted position. Another method is to analyse the air in a bottle containing nearly 1 per cent. of carbon dioxide, and compare the results with those given by the large apparatus with the same bottle of air.

The following examples will serve to illustrate the degree of accuracy attainable with the apparatus. The results are in volumes per 10,000.

I. *Six successive samples of outside air (winter).*

(1) 2·8. (2) 3·2. (3) 3·3. (4) 2·7. (5) 3·3. (6) 2·8.
Mean, 3·0.

II. *Three bottles of same outside air, collected in bottles.*

(1) 2·6. (2) 3·3. (3) 2·9. Mean, 2·9.

III. *Six successive analyses of air in same bottle of vitiated air.*

(1) 16·6. (2) 16·0. (3) 16·4. (4) 16·2. (5) 15·6. (6) 15·8.
Mean, 16·1.

IV. *Three successive analyses of samples from same bottle of vitiated air.*

(1) 51·0. (2) 50·8. (3) 51·4. Mean, 51·1.

These examples show that with ordinary care the analysis may, after some practice, be relied on to within 0·5 volume per 10,000 on either side of the correct result.

The following experiments may be quoted in connection with the reliability of the method of collecting samples of air in bottles in the manner already described and keeping them for some days for analysis.

I. Four samples of outside air collected simultaneously in dry and clean bottles were kept for varying periods and then analysed. The results were as follows in volumes of CO₂ per 10,000 volumes of air:—

Bottle (1), analysed at once	.	.	{ (a) 3·0
			{ (b) 3·0
„ (2) „ after 5 days	.	.	2·8
„ (3) „ „ 9 „	.	.	3·0
„ (4) „ „ 19 „	.	.	{ (a) 2·8
			{ (b) 3·0

II. Five bottles of air collected simultaneously in dry and clean bottles in a room containing vitiated air were similarly kept and analysed.

Bottle (1), analysed at once	.	.	{ (a) 51·0
			{ (b) 51·4
			{ (c) 50·8
„ (2) „ „	.	.	50·8
„ (3) „ after 2 days	.	.	51·2
„ (4) „ „ 6 „	.	.	{ (a) 50·7
			{ (b) 51·0
„ (5) „ „ 14 „	.	.	{ (a) 50·6
			{ (b) 50·4

III. Four samples of outside air were collected in bottles which were both wet and dirty from dust purposely introduced.

Bottle (1), analysed at once	.	.	3.0
„ (2) „ after 2 days	.	.	2.8
„ (3) „ „ 6 „	.	{ (a)	8.0
		{ (b)	7.6
„ (4) „ „ 12 „	.	.	15.0

IV. Five samples of outside air were collected in bottles which were dirty from dust purposely introduced, but dry.

Bottle (1), analysed at once	.	.	3.0
„ (2) „ after 2 days	.	.	3.2
„ (3) „ „ 6 „	.	{ (a)	3.2
		{ (b)	3.0
„ (4) „ „ 12 „	.	.	3.0
„ (5) „ „ 17 „	.	.	2.8

V. Four samples of outside air were collected in bottles which were clean but wet.

Bottle (1), analysed at once	.	.	3.0
„ (2) „ after 3 days	.	{ (a)	2.4
		{ (b)	2.2
„ (3) „ „ 5 „	.	{ (a)	2.0
		{ (b)	2.6
„ (4) „ „ 12 „	.	{ (a)	0.2
		{ (b)	0.0

VI. Four samples of vitiated air were collected

simultaneously, two being in clean and dry bottles and two in clean and wet bottles.

Dry.

Bottle (1), analysed at once	.	.	{ (a) 20·6
			{ (b) 20·8
„ (2) „ after 9 days	.	.	{ (a) 21·2
			{ (b) 21·2

Wet.

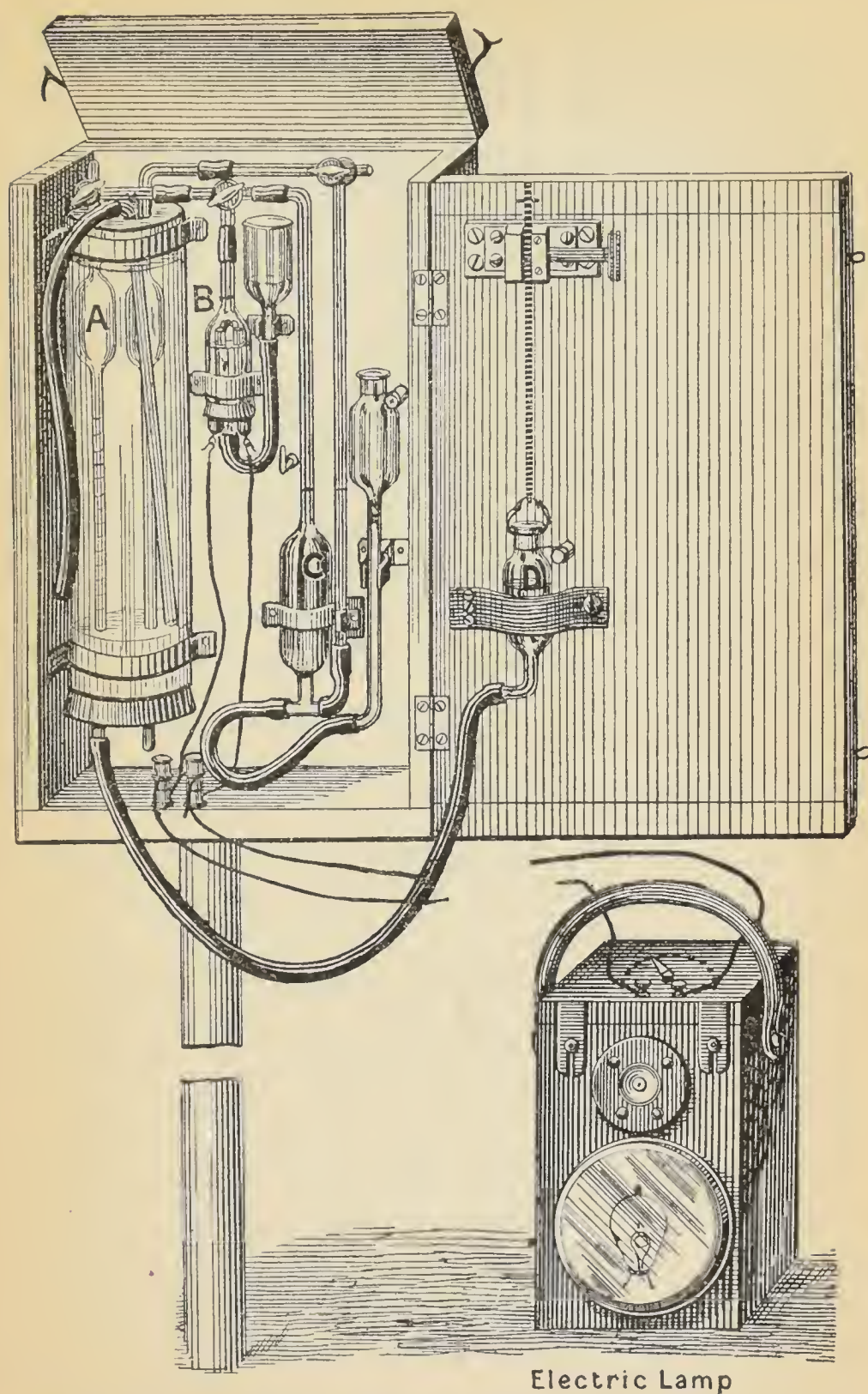
„ (3) „ at once	.	.	{ (a) 21·0
			{ (b) 20·4
„ (4) „ after 9 days	.	.	{ (a) 18·6
			{ (b) 18·8

These experiments show that in clean and dry bottles, with stoppers properly greased with vaseline, samples of air will keep perfectly for long periods, but that in wet bottles, whether clean or not, the percentage of carbon dioxide alters. If the bottle is wet and dirty, the carbon dioxide may increase greatly owing to bacterial action. If the bottle is wet and clean, carbon dioxide may disappear owing to the presence of alkali dissolved from the glass. Samples collected by the old method of emptying a bottleful of water are quite unreliable so far as carbon dioxide is concerned. During the process of emptying the air may either take up carbon dioxide from the water or give it up to the water, and the proportion of carbon dioxide inside the bottle may alter afterwards in the wet bottle.

PORTABLE APPARATUS FOR DETERMINING CARBON DIOXIDE, METHANE, OR CARBON MONOXIDE AT MINES WORKED WITH NAKED LIGHTS.

IN metalliferous mines or coal-mines working with naked lights it may be desirable to determine the proportion of methane or carbon dioxide in air-ways or working places, or of carbon monoxide after blasting in working places. The proportions present of these gases are small, and the apparatus shown in fig. 13 has been designed with a view to their convenient determination, either underground or on surface. It may, for instance, be desired to determine on the spot how much carbon dioxide is present in the air at different points, or how much methane is present in air which does not show a cap on the flame of a safety-lamp, or whether an explosive leaves any serious proportion of carbon monoxide in the air after blasting.

The apparatus is on the same principle as that already described (p. 47), except that it is smaller and more compact, and does not afford a means of determining oxygen or any high percentage of other gases. It is enclosed in a wooden case, the internal dimensions of which are $7 \times 12 \times 2\frac{1}{2}$ inches. The weight, when the whole is ready for use, is



Electric Lamp

FIG. 13.—Portable Apparatus for Carbon Dioxide, Carbon Monoxide, and Methane, in Naked-light Mines.

about $5\frac{1}{2}$ pounds. The air-burette A, which is enclosed in a glass water-jacket, consists of a wide ungraduated and a narrow graduated portion. It holds 10 c.c. from the tap to the bottom of the scale. The graduated portion, which is 4 inches long, is divided into about 100 divisions, each of which corresponds to $\frac{1}{5000}$ th part of the volume of the burette. The lowest division is marked 0, and the highest 200, if exactly 100 divisions are present. Each division on the burette thus counts for two on the scale. Any difference between a reading at or near zero and a second reading is thus shown by the scale in volumes per 10,000, there being no calculations. A difference of 100 on the scale would therefore correspond to 1 per cent. The diameter of the potash pipette C, and of the combustion pipette B, is 1 inch, and the length 2 inches. The connecting tubes leading to these pipettes, and to the pressure gauge of the control tube, have an internal diameter of 1.8 to 2.2 mm.; but the rubber and glass tubes leading onwards from the potash pipette to the reservoir is about 4 mm. in bore. The potash reservoir slides up and down on a spring clamp, and the mercury reservoir D is suspended from a hook attached to the rack-and-pinion apparatus shown.

The general mode of using the apparatus is exactly the same as with the larger apparatus; the same precautions are needed, and the apparatus should be tested in the same way (see pp. 39–42). The efficient working of the apparatus can be ascertained by depriving a sample of outside air of carbon dioxide, and seeing that

its volume as read off is not altered by as much as .01 per cent. after it has been passed over into the potash pipette or combustion pipette with the spiral heated. Any leakage, obstruction, or absorption of oxygen by the potash solution, or other source of error, would thus be revealed.

In connection with work underground it is particularly important to realise the importance of closing the connections between the potash and the gas-burette and control tube at the end of each analysis. If this precaution is neglected, and the apparatus meanwhile taken down a shaft, or from a return to an intake road, or from any very warm place to a cool one, the potash may be driven over into the burette, and the apparatus thus rendered useless until it has been thoroughly washed out with dilute acid. If this accident has happened the taps will jam unless they are washed out within a few hours.

As it may be difficult to find convenient places underground on which to set the apparatus during an analysis, a brass socket is provided in the bottom of the case, into which the brass top of a wooden rod about 4½ feet long can be screwed. The apparatus can then be allowed to lean against the side of a road or working place during an analysis, and the readings can be made quite conveniently by the light of a candle or lamp, or of a pocket electric lamp carried for the purpose.

When the apparatus is used for analysing bottle samples above-ground, a mercury trough and curved tube with additional three-way tap must be employed

as in the case of the apparatus for determining small percentages of carbon dioxide (p. 67).

Process of Analysis.—After adjusting the potash level the mercury reservoir is raised so as to expel all air from the burette to the outside. The tap of the burette is then closed by turning it one-eighth round, and the reservoir replaced on the hook at the right level for filling the burette. The apparatus is then carried open to the point from which the sample is required (unless it is already at this point), and the tap opened so as to allow the burette to fill. The tap is then again closed, and the apparatus placed in position for the analysis. After roughly levelling the mercury in the burette and reservoir the taps of the burette and control tube are opened towards the potash solution, and the potash levels adjusted exactly to the marks after blowing air through the water-jacket. A reading is then taken, and ought, of course, to be close to the zero-point of the graduations. The carbon dioxide is then absorbed, as in the larger forms of apparatus, and a second reading taken after again blowing air through the water-jacket and carefully adjusting the levels. The difference between the two readings gives the proportion of carbon dioxide in volumes per 10,000.

The air is then passed into the combustion pipette and back several times, while the platinum spiral is heated to whiteness by a current from a hand electric lamp or other source. After this process is complete a short time should be given for the glass to cool, before adjusting the levels and reading off the contraction.

The carbon dioxide formed is then also determined in the usual way. The results indicate the nature and percentage of any combustible gas present. It is evident, however, that if the carbon dioxide is determined first, as just described, a small part of the combustible gas will be left in the connections between the tap of the combustion pipette and the potash pipette. The percentage correction for this space may be determined once for all by making a determination of the combustible gas in a sample without washing out this space, and determining the addition found on washing out the space.

After an analysis the mercury reservoir is fixed to the case by a piece of leather, or elastic webbing, as shown in the figure.

The apparatus as described above is not designed for use underground in mines where much fire-damp is present, and safety-lamps are needed, as a mistake in turning the switch might possibly cause a spark, although this could do no harm at any place where a safety-lamp still burned. The burette is also too narrow for determinations of methane, if more than 1 per cent. is present. If the apparatus is required for the analysis of bottle samples of air from a fiery mine, or for analysis underground at places where there would be no risk from accidental sparking, a burette ten times coarser is employed. Each division on the scale corresponds to $\frac{1}{1000}$ th part of the capacity of the burette. The lowest of the hundred divisions is marked 0, and the highest 10, so that each division counts for 0.1 on the scale, or

0.1 per cent. The coarse burette must be ordered specially, and may easily be substituted for the ordinary finer one.

The following examples will serve to illustrate the use of the apparatus:—

1. *Air from an "End" in a Metalliferous Mine, shortly after shot-firing with gelignite. Finer burette used.*

First reading of burette 6

After CO_2 absorbed 82

—
 $\therefore \text{CO}_2$ in volumes per 10,000 = 76 = 0.76 per cent.

After combustion 86

—
 \therefore contraction = 4

After CO_2 absorbed 92

—
 $\therefore \text{CO}_2$ produced = 6 = 0.06 per cent.

When calculated out in the ordinary way, and in view of the fact that carbon monoxide and hydrogen are practically the only combustible gases formed in the explosion of gelignite, the results are:—

Carbon dioxide 0.76 per cent.

Carbon monoxide 0.06 „

Hydrogen 0.007 „

As, however, an addition to the percentage of combustible gas of 7 per cent. was needed, because some of the gas was left unburnt in the dead space beyond the combustion pipette, the corrected result was .064 per cent. of carbon monoxide and .007 per cent. of hydrogen.

2. *Air from a Return Air-way in a Naked Light Colliery. Only methane determined.*

First reading of burette . 11

After combustion . . 77

$$\therefore \text{contraction} = \frac{66}{\text{---}} = 0.33 \text{ per cent. of methane.}$$

There was no correction to be made, as the air was not passed into the potash pipette at all.

3. *Air from a Return Air-way in a "Fiery" Colliery. Coarse burette used.*

First reading of burette . 0.22

After CO₂ absorbed . . 0.54

$$\therefore \text{CO}_2 = \frac{\text{---}}{\text{---}} = 0.32 \text{ per cent.}$$

After combustion . . 4.60

$$\therefore \text{contraction} = \frac{4.06}{\text{---}} = 2.03 \text{ per cent. of CH}_4.$$

Adding 7 per cent. for the dead space, the methane percentage was 2.17.

PORTABLE APPARATUS FOR ROUTINE FIRE-DAMP ESTIMATIONS.

THE various forms of apparatus described above require considerable skill and practice in use, and may easily get out of order unless they are used with care. The potash, for instance, is liable to be sucked over, foul the apparatus, and jam the taps. The following apparatus has therefore been designed for use by persons who have not the time to devote to delicate apparatus or analyses of the highest accuracy, but who wish to ascertain as rapidly and simply as possible the percentage of methane in ordinary open air-ways or working places in a colliery, or at any point where a lamp burns.

The apparatus is shown in fig. 14.¹ It is enclosed in a stout case measuring $13 \times 11 \times 3$ inches, and consists of an air-burette, combustion pipette, and primary cell for furnishing a current to heat the platinum spiral. Potash solution is entirely dispensed with, and the percentage of fire-damp is given simply by measurement of the contraction on combustion.

¹ The illustration is from an early model of the apparatus, and does not show various minor improvements afterwards introduced.

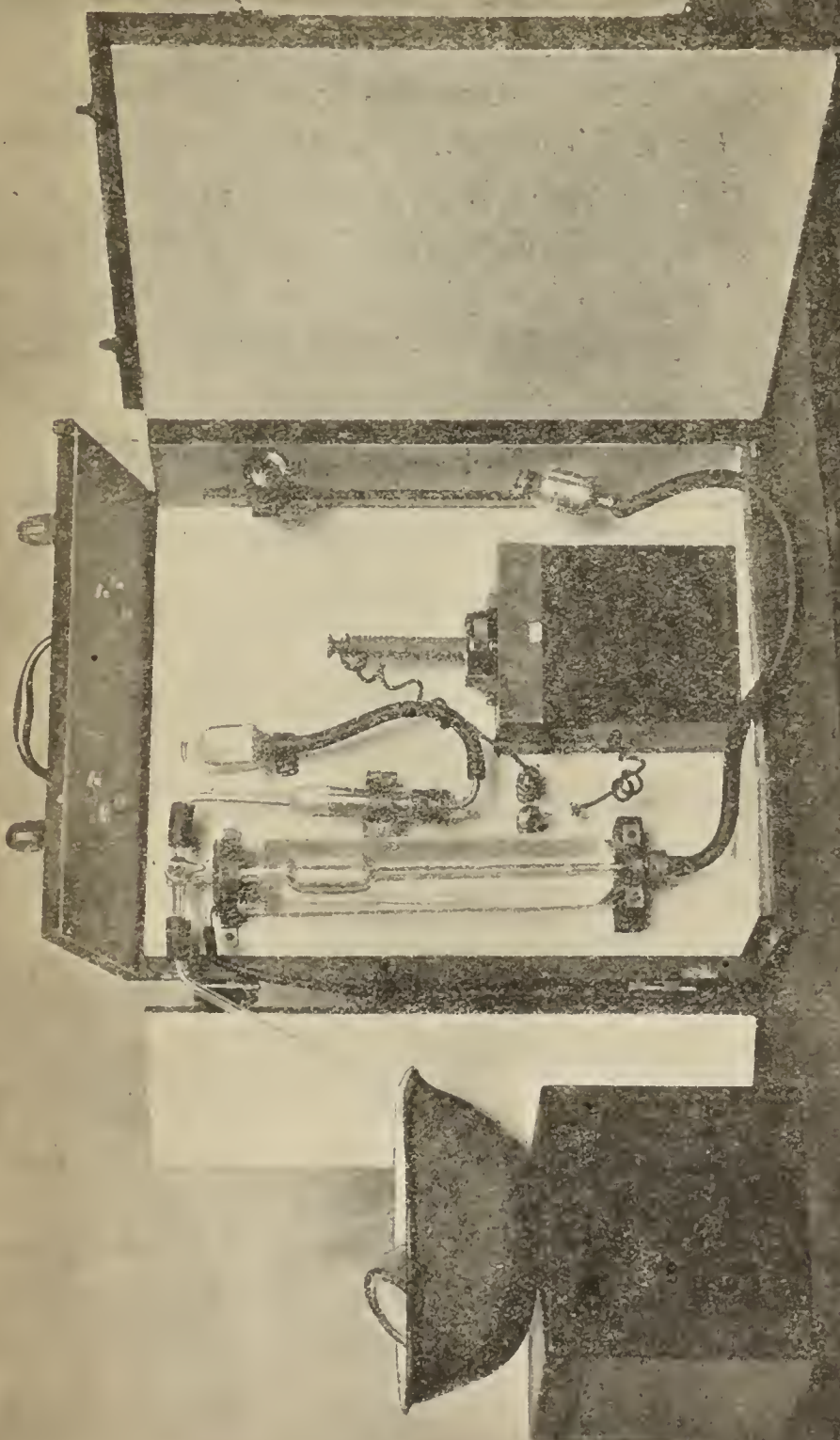


FIG. 14. — Portable Apparatus for Routine Fire-damp Estimations.

The burette holds 10 c.c., and the stem is divided into fifty parts, each of which corresponds to $\frac{1}{500}$ of the total capacity. The numbering is from 0 at the bottom to 6 at the top, and each whole number corresponds to the contraction produced by 1 per cent. of methane, so that the burette indicates directly the percentage of methane. Air which is explosive from the presence of more than 6 per cent. of methane cannot be analysed, as the stem of the burette is too short.

The combustion pipette is so arranged that a short piece of fine platinum wire is stretched between the free ends of the stout platinum wire which passes up, through glass tubing with fused ends, into the combustion pipette. This short and fine wire is very easily heated, so that a sufficient current is afforded by a small cell. The cork of the combustion pipette is held firmly in position by a support, so that it cannot be blown out by an explosion.

The current is furnished by a bichromate cell, so arranged that the zinc is ordinarily held clear of the bichromate, and only becomes immersed when a rod attached to it is screwed downwards. The amount of current is regulated by the degree to which the zinc is immersed in the bichromate, so that a rheostat is not needed.¹ Sparking is also impossible, which makes the cell safe in a fiery mine, though it should never be used at any place where the air is liable to become explosive.

In using the apparatus in a mine the mercury in the

¹ This arrangement of the cell was suggested by Sir Henry Cunynghame, Chairman of the Royal Commission on Mines.

combustion pipette is first brought to the mark (where it should stand when the pressure in the burette is atmospheric); the burette is then filled with mercury to the outlet, the tap closed, and the reservoir replaced at the level required for completely filling the burette. On opening the tap the sample is sucked in. The tap is then turned so as to connect the burette with the combustion pipette, and the mercury in the latter brought exactly to the mark, after blowing through the water-jacket to mix the water. The burette is then read off. The whole of the sample is now passed into the combustion pipette by raising the mercury reservoir. When the mercury has reached the tap, the latter is closed and the reservoir replaced. The rod of the bichromate cell is now depressed cautiously until the platinum wire gradually becomes white hot, and the wire is kept at a bright white heat for one minute while some of the air is passed back and forward from the burette to the combustion pipette. One minute or less is sufficient to burn all the methane. After this the rod of the cell is screwed completely up and the air passed back into the burette and again measured after blowing through the water and bringing the mercury in the pipette to the mark exactly. The temperature in the jacket ought not to have altered more than one degree F. during the combustion, but if the apparatus has just been moved to a warmer or cooler place it may be well to make certain of this by keeping a thermometer in the jacket. The difference in the readings before and after the combustion gives the percentage of methane. A

second reading may be made after a second combustion, if there is any doubt as to the wire having been hot enough to complete the combustion. A bright heat is necessary for the rapid combustion of methane, and the cell must be re-charged if the wire is not white hot.

As there is no control tube, and the mercury level is a much less sensitive index of pressure than the level of potash solution, the accuracy attainable with this apparatus is considerably less than with that previously described; but the error ought not to exceed 0.1 per cent. in a determination of methane. A rise of 1° F. in the water-jacket during the analysis would make the result about 0.1 per cent. too low; and conversely for a fall of 1° . The burette must be kept moist inside.

When the apparatus is used to analyse bottle samples, a curved tube (shown in fig. 14) is attached to the burette and cautiously filled with mercury by raising the reservoir with the tap only partly open. The sample is then opened under water in a bowl, the tube inserted into the bottle, and the burette filled with the air. The curved tube keeps the bottle in position while the burette is filling; and in case it should be necessary to repeat the analysis, the stopper should be again inserted under water, so that the residual air can be discharged from the burette and curved tube before the second sample is taken in.

The apparatus is provided with a rod which screws into the bottom of the case and serves to support it at a convenient height while it is leant against the side of a roadway or working place underground. The battery

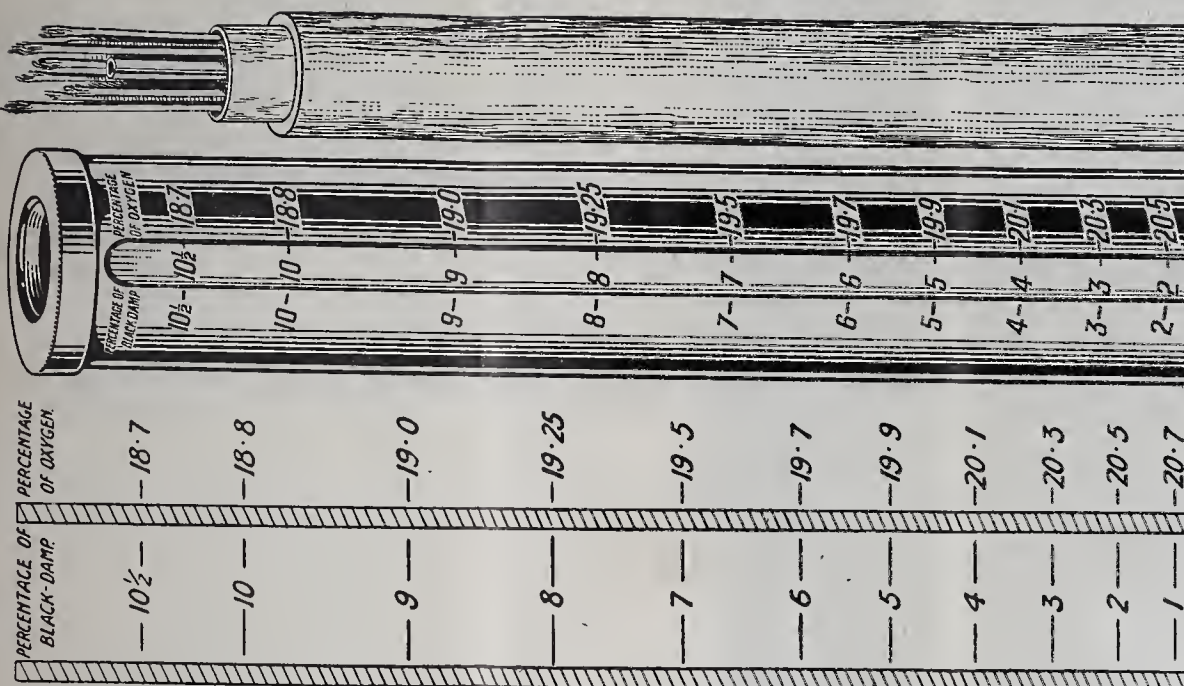
can be re-charged at any time by dissolving in the required volume of water two of the powders supplied by the makers along with the cell. If the piece of thin platinum wire fuses it can easily be replaced, and a spare piece should be kept for this purpose. The apparatus must not be laid on its side unless the cell has been emptied and the mercury reservoirs corked up. For work in an office or laboratory it will save trouble to take the current from a small accumulator, or dry cells, or from the lighting current, through a rheostat, in the manner already described (p. 16). An ordinary platinum spiral, made from a longer piece of wire, can then be used, and shortens the process considerably.

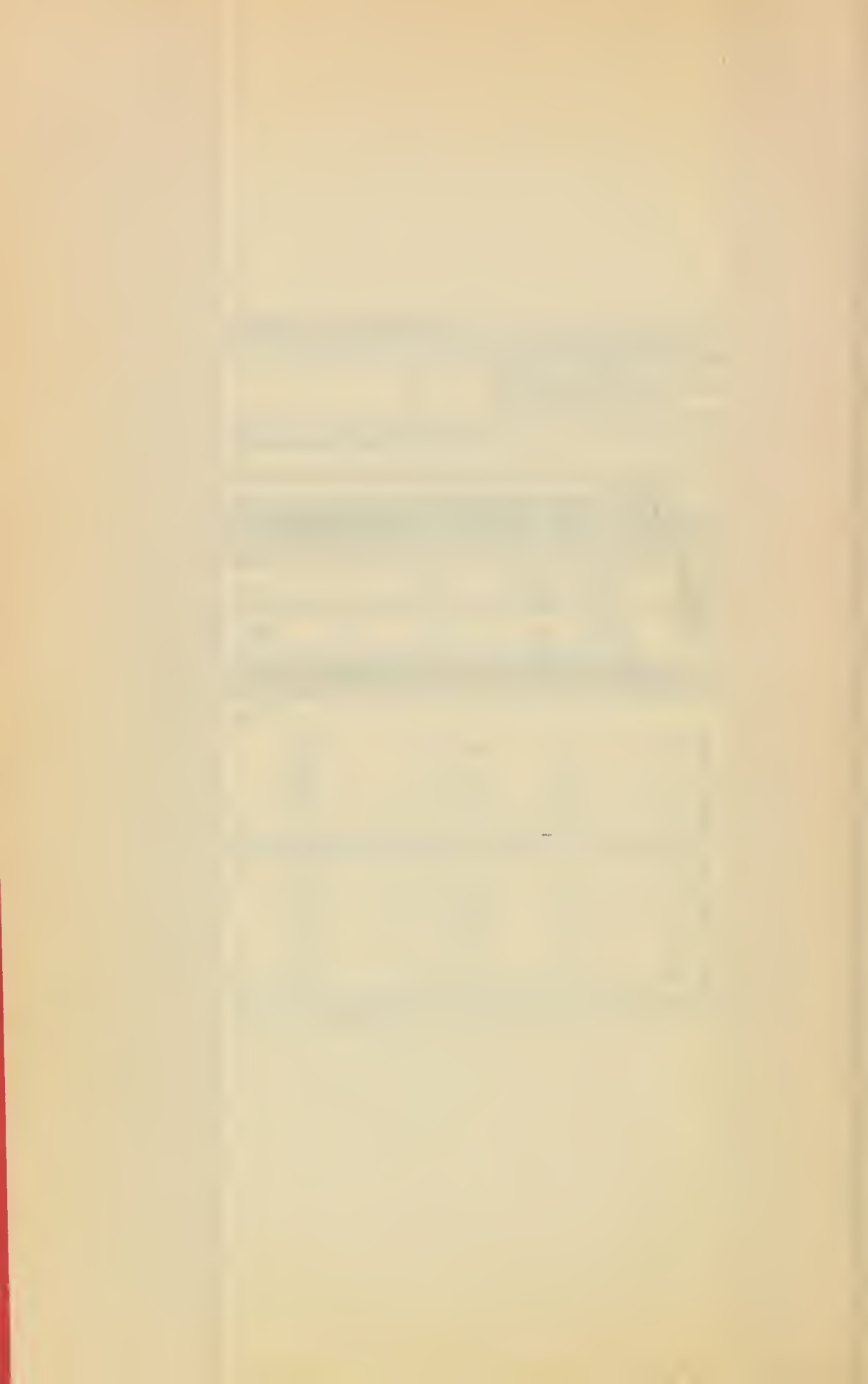
APPARATUS FOR APPROXIMATE DETERMINATION OF OXYGEN BY FLAME TEST.

A FLAME of any kind is extremely sensitive to variations in the percentage of oxygen in air. Both the light given by a flame and the ease with which it can be extinguished by a current of air are greatly affected. Variations in atmospheric pressure (and consequently in the partial pressure of oxygen) have, on the other hand, only a comparatively small influence on the flame. The following method¹ for approximately determining the oxygen percentage in air is based on the fact that as the oxygen percentage in air diminishes the flame is extinguished more and more easily by a current of air.

The apparatus consists of some thin tapers and a stout glass tube 7 inches long and 0.75 inch in internal diameter, graduated as shown in fig. 15. To protect the glass from accident it is enclosed in the aluminium case shown in fig. 16, the scale being marked on the case, in addition to marks on the enclosed glass. The length of the case is exactly 7 inches, and the openings at the top and bottom of the case are 0.75 inch in

¹ Originally described in the *Transactions of the Institution of Mining Engineers*, vol. xli. p. 455, 1911.





diameter. The glass itself is slightly less than 7 inches long. Between the case and the glass there is a thin sheet of asbestos cloth, and washers are also provided between the metal caps and the ends of the glass to further protect the glass should the tube be accidentally dropped. A supply of tapers is carried in a wooden case (fig. 17) which fits inside the tube, and along with the tapers there is a brass holder, with the help of which a lighted taper can, if necessary, be lowered into the tube. The holder also makes it possible to use up quite short pieces of taper. The tube is carried about in an outer case of japanned metal, which keeps the wooden case in position.

When a lighted taper is held vertically inside the tube an upward draught is, of course, produced by the heat; and this draught varies in strength, according as the taper is held high up or low down in the tube. The draught tends to blow the flame out; and according to the percentage of oxygen in the air, the flame is extinguished at a point lower down or higher up in the tube. The position of the graduation marks was empirically determined by experiments in a closed chamber, the air of which was vitiated by respiration or by gas burning. One scale gives the oxygen percentage, and the other the percentage of what is familiarly known to miners as "black-damp." The latter is simply the residual gas (a mixture with an average composition of about 87 per cent. of nitrogen and 13 per cent. of carbon dioxide) left by oxidation processes in the mine. It is evident that the percentage of "black-damp" in

mine air is determined (provided that methane or other gases are absent) by the percentage of oxygen. Hence the two scales run parallel. The "black-damp" scale is marked on the glass, as being more simple than the oxygen scale; but the latter scale need alone be considered here.

The lowest oxygen percentage marked on the scale is 18·7. Below about this percentage the taper will no longer burn in the tube, and, when held outside the tube, it will not burn in a vertical position with less than 18·2 per cent. of oxygen; but when held horizontally it will still burn until the oxygen has fallen to 17·2 per cent. There is thus a wide range within which the oxygen percentage may be estimated by the taper-and-tube method.

As the flame becomes very small when it is just on the point of extinction, its position with respect to the graduations on the tube can be determined quite easily. The lighted taper should first be pushed up to a point where it burns easily, and then gradually lowered. With a little practice it is easy to find with considerable exactness the point at which it is just extinguished. Care must be taken not to breathe across the lower end of the tube while the observation is being made. If the air is much vitiated, it may be necessary to push the taper (held in the brass holder) through the tube before lighting it, and then to lower it cautiously into the tube.

The tapers used for graduating the tube, and supplied with it by the makers, are white wax tapers $\frac{1}{8}$ of an inch in diameter. Other tapers give, however, nearly

the same result, though thick ones are less convenient and may crack the glass. An ordinary wax match with the head removed answers well enough when held in the brass holder.

There are several other circumstances, besides the oxygen percentage as revealed by ordinary analysis, which affect the results to some extent. The chief of these is the percentage of aqueous vapour in the air. An ordinary chemical analysis gives the percentage of oxygen in the air when absolutely dry—a condition never met with outside a laboratory. The actual percentage of oxygen by volume in ordinary air is, of course less than 20·93, because the air is diluted to some extent by aqueous vapour; and on an average outside air in England is mixed with about 1 per cent. of aqueous vapour, which reduces the real oxygen percentage by a hundredth, that is from 20·93 to 20·72. The flame reacts approximately to the real oxygen percentage, and it will thus be understood readily that the more moisture is present in the air the lower will be the oxygen percentage given by the test. Mine air contains on an average about 2 per cent. of moisture, and about as much moisture is likely to be present in most cases where the tube method would be of use. For this reason the tube was graduated with air containing 2 per cent. of moisture, which corresponds to saturation with moisture at about 64° F. (see p. 112). Except in warm and moist weather, therefore, the flame will not go out at the zero-point of the graduations when a test is made in pure air.

The indications are not appreciably affected by such

variations of atmospheric pressure as occur on the surface in England; but at depths or altitudes of more than 2000 feet from sea-level the readings need some correction. Thus at a depth of 3000 feet, with the barometer at about 33 inches, the indications were found to be about 0·2 per cent. too high; and with increasing height above sea-level the indications become increasingly too low. At a height of 14,100 feet and a barometric pressure of 18 inches (on the summit of Pike's Peak, Colorado) the indications were about 1·2 per cent. too low.

The following experiments (made in air saturated with moisture at about 64°) illustrate the somewhat surprising accuracy with which the oxygen percentage can be determined by means of the tube and taper when there are no disturbing conditions. It must, however, be borne in mind that such conditions (varying air currents, barometric pressures, and percentages of moisture) are usually present to some extent when this method is employed in mines, etc.

Percentage of Oxygen.		Percentage of Carbon Dioxide
Indicated by Tube.	Found by Analysis.	
20·90	20·90	0·06
20·45	20·33	0·49
20·15	20·13	0·65
20 00	20·07	0·71
19·65	19·63	1·07
19·25	19·32	1·33

This means of testing is not applicable in mines where safety-lamps are required; but in mines, etc., where the method can be used, and the percentage of aqueous vapour and barometric pressure are not abnormally high or low, the results are reliable to within about 0·2 per cent. The advantage of the method is that it is very rapid and simple. It does not indicate the carbon dioxide percentage directly, but this can be inferred with tolerable accuracy in a mine if the usual ratio between excess of carbon dioxide and deficiency of oxygen has once been ascertained by analysis. If, for instance, this ratio was known from analyses to be about 3 to 4 (a common ratio in metalliferous mines), and the oxygen percentage indicated by the tube was 19·3, or 1·6 per cent. below the proportion in pure air, the carbon dioxide percentage would be about $1·6 \times \frac{3}{4} = 1·2$ per cent.

Briggs' Safety-lamp Method.—The method described above is of course not applicable in mines where safety-lamps have to be used. In order to meet this difficulty Dr Henry Briggs has recently devised an arrangement which can be used with a safety-lamp. A full description is given at page 169, vol. li., of the *Transactions of the Institution of Mining Engineers*. The principle of the arrangement is that by means of an adjustable graduated cut-off the air-supply to the lamp is cut down until the flame is just on the point of extinction. The amount to which the cut-off must be adjusted varies with the oxygen percentage of the air, and the cut-off is graduated accordingly.

An accuracy of the same order as that of the tube

method can be reached with the Briggs' lamp method. Moisture and barometric pressure influence the lamp readings in the same way as those of the tube. The presence of fire-damp in the air makes the readings slightly too high. To correct for fire-damp the percentage of the latter must be estimated by the cap method described below. A fifth of the percentage of fire-damp is then deducted from the percentage of oxygen which has been indicated by the lamp.

The lamp method is very useful to firemen in ascertaining whether the air contains the minimum percentage of oxygen allowed by the Coal Mines Act (19 per cent.). The cut-off is simply set to 19 per cent.; and if the flame does not threaten to go out, the fireman knows at once that the air complies with the standard.

APPROXIMATE ESTIMATION OF METHANE, ETC., BY FLAME TEST.

WHEN methane or any other combustible gas or vapour is present in air in proportions not sufficient to form an explosive mixture a zone of combustion extends above the limits of the ordinary flame, manifesting its presence by the appearance, under favourable optical conditions, of a pale "cap" on the flame. With increasing percentages of the combustible gas the cap becomes more and more luminous, and later increases rapidly in height. When the mixture is just inflammable, the cap may be said to have increased to a size only limited by the extent of the inflammable atmosphere.

It must be clearly understood that the cap itself is one thing, and its visibility another. When the flame itself is luminous, the cap may be invisible because the excitation of the retina at the point on which the image of the flame falls diminishes enormously the excitability of the adjoining part on which the image of the cap falls. It is only, therefore, when the cap is long and relatively luminous, and the air nearly inflammable, that a cap is visible on a luminous flame. Nevertheless, it is quite easy to photograph the invisible cap on a luminous flame, as has recently been shown by Messrs E. B. Whalley and

W. M. Tweedie; and the heating of the gauze in the chimney of a safety-lamp to redness may also furnish unpleasant evidence of the existence of a cap.

It should also be understood that the height of the actual cap depends on the size, or perhaps rather the height, and the temperature of the flame. There is thus no definite ratio between height of cap and percentage of inflammable gas, unless the flame is of a standard height and temperature. The relatively long and very hot flame of a jet of hydrogen will give a longer cap than a small blue oil flame with fifteen times as much methane in the air.

The presence of the cap on the flame affords an invaluable means of estimating, with an ordinary oil flame, the percentage of methane in the air of a mine, or, more generally, the approach towards inflammability of any mixture of a combustible gas with air. A mixture of methane with air becomes just inflammable when 6 per cent. of methane is present, while the cap on the oil flame of a miner's safety-lamp can, with proper care, be observed with all percentages from 1 up to the point of inflammability.

It will be sufficient to describe here the method of testing for methane with an ordinary safety-lamp and the ordinary burner, burning the ordinary mixture of "colza" and paraffin oil. To test for methane, the flame of the lamp is cautiously pulled down until only a very slightly luminous tip is left on the flame, which is about a tenth of an inch high. If 1 per cent. or more of methane is present in the air a cap, or part of one, will be visible

above the flame. Fig. 18, which is constructed from a series of plates from observations and sketches made by Sir John Cadman,¹ the percentages of methane being accurately determined by analysis, shows in full size the outlines of the burner, the testing flame, and the visible caps. It will be seen that with 1 per cent. only the base of the cap can be seen. With $1\frac{1}{2}$ per cent. most

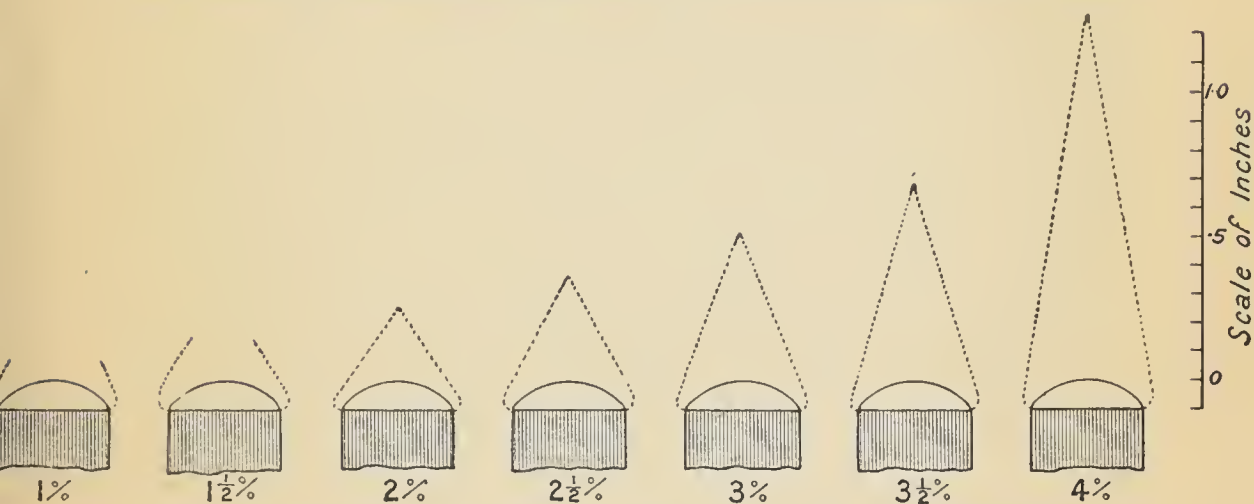


FIG. 18.—Diagram showing Outlines of Caps Visible on an Oil Flame with Different Percentages of Methane.

of the cap is visible, but the tip fades into invisibility. At 2 per cent. the tip is just visible, and with increasing percentages the height of the cap increases in a rapidly increasing ratio. The diagram does not show, however, the fact that the luminosity of the cap increases steadily from the lower percentages upwards. It is by the luminosity and the visibility of the tip, rather than by the height of the cap, that the percentage of methane can best be gauged up to 3 per cent. It is very

¹ *Reports on Mine Ventilation and on Methods of determining Fire-damp*, by Professor Cadman and Mr E. B. Whalley, Parliamentary Paper [Cd. 4551], 1909.

important to note that the tip is just visible at 2 per cent.

In testing for fire-damp by the method just described there is considerable risk of the flame going out; and to obviate this, and increase the delicacy of the test, Sir Henry Cunynghame and Professor Cadman have introduced a device by which the cap on a full flame can be rendered luminous by sodium vapour, so that the test can be made with a full flame.¹

A still simpler method of rendering the cap visible on a full flame has been described by Mr H. Briggs (*Trans. Inst. of Mining Engineers*, 1912). By introducing a loop of copper wire into the flame the latter's luminosity is so much diminished that the cap is made easily visible. The same loop can also be employed to indicate whether the oxygen percentage in the air is above or below 19 per cent. The presence of fire-damp interferes with this latter test, however.

The most delicate cap test for fire-damp, etc., is that with the hydrogen flame; and by means of the Clowes hydrogen testing lamp it is possible to detect as little as 0.2 per cent. of methane. The cap with this percentage is very pale, but can be seen to extend about 0.6 inch above the tip of the standard hydrogen flame.

¹ *Trans. Inst. of Mining Engineers*, vol. xxxix. p. 13.

GRAVIMETRIC DETERMINATION OF MOISTURE AND CARBON DIOXIDE IN AIR.

IN some cases it is necessary to determine with great accuracy the amount of carbon dioxide or aqueous vapour, or of both, in air; and for this purpose it may be desirable to use the gravimetric method, although usually the moisture can be estimated with sufficient closeness from dry- and wet-bulb thermometer readings, and carbon dioxide by ordinary gas analysis, as described above. The gravimetric method is required more particularly in certain kinds of physiological work, where moisture and carbon dioxide have to be determined together; and the apparatus¹ now to be described was designed with a special view to physiological investigations, although it is equally suitable for other work in which great accuracy is essential.

Determination of Moisture.—The absorption apparatus (together with that for carbon dioxide) is shown in fig. 19. It consists of a pair of thin glass test-tubes, *a, a*, containing pumice soaked in sulphuric acid. Each tube measures 4×1 inch, and is provided with a double-bored cork about $\frac{1}{2}$ inch thick, which is fitted with glass tubing of about $\frac{3}{16}$ inch internal diameter, and in the

¹ Haldane and Pembrey, *Philosophical Magazine*, 1890, p. 306.

form shown in the figure. The longer piece of tubing in the first tube should be made shorter than the corresponding piece in the second tube, in order to avoid resistance caused by the accumulation of water. The tubing must fit firmly. The corks are covered with a layer of paraffin wax inside and out. They are pushed down flush with the tops of the tubes, the end of each tube being first very carefully wiped inside free of acid,

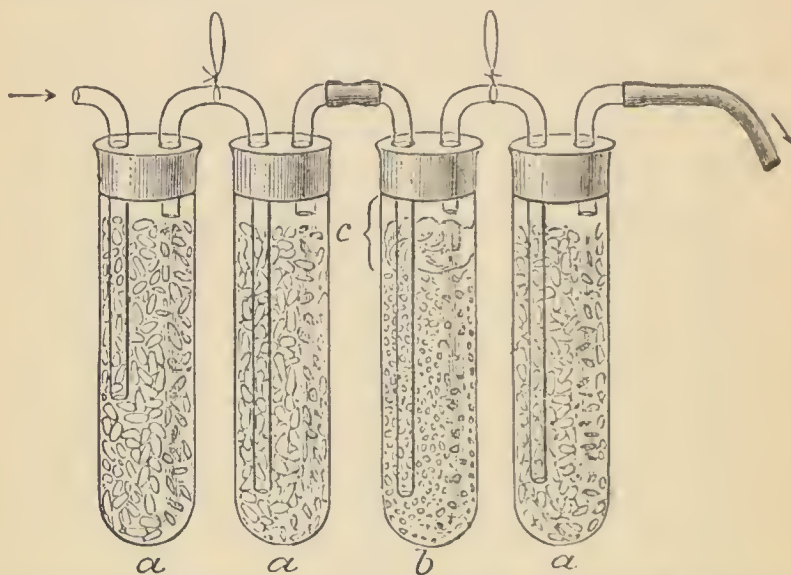


FIG. 19.—Absorption Tubes for Determination of Moisture and Carbon Dioxide in Air.

and then warmed to soften the paraffin on the cork and so facilitate its entrance. To enable the longer limb of the tubing to be pushed down, a passage should first be cleared in the pumice with a glass rod. A layer of paraffin is spread smoothly over the top of the cork. The apparatus must be absolutely tight, and should allow air to pass quite freely when suction is applied. It should be carefully cleaned with a wet cloth to remove any trace of acid, and then dried.

The fragments of pumice are sifted through a sieve with about seven meshes to the inch, and shaken on a fine one to remove the powder. They are then heated to redness with a large blow-pipe flame, and thrown, still hot, into pure re-distilled sulphuric acid. The superfluous acid is then poured off, and the pumice preserved in a stoppered bottle, from which the tubes are filled. Before using the tubes they should be washed out with air, to remove traces of sulphurous acid. Each pair of tubes weighs, when filled, about 80 grammes.

To diminish to a minimum the errors arising from accidental variations in weight of the tubes, the weighing is always done against a counterpoise consisting of a similar pair of absorption tubes, always kept in the same place. Since, during an experiment, the absorption tubes will have been warmed above the temperature of the counterpoise, the weighing must be deferred for half an hour, so as to allow their temperatures to become equal again. The tubes are provided with stoppers consisting of a short piece of rubber tubing, closed at one end with a piece of glass rod. The weighing is done without stoppers, and if several tubes are to be weighed, the stoppers are removed from the whole of them, including the counterpoise, and not replaced till the last has been weighed. No absorbent for moisture is kept inside the balance case. The tubes should be lifted by the wires attached to them for hanging on the balance.

Numerous experiments have shown that the absorption of moisture by one of these pairs of tubes is com-

plete, even with very rapid currents of air. Thus with two pairs in series and the air passing through at the extremely fast rate of 7 litres per minute, the increase of weight was as follows after 21 litres of air had passed:—

Pair (1) +0.2142 gramme

Pair (2) +0.0001 „

With a rate of 1 litre per minute the absorption by

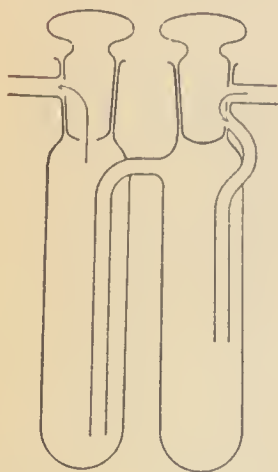


FIG. 20. — Improved Form of Absorption Tubes for Moisture and Carbon Dioxide.

the first pair was still perfect after 13 grammes of moisture had been absorbed from 2300 litres of air. The first tube had then become blocked by dilute acid, so that the experiment had to be stopped.

The tubes should be weighed to decimilligrammes, and by using the counterpoise the errors of weighing are reduced to a maximum of 3 decimilligrammes. Without the counterpoise they are about ten times as great.

The use of paraffined corks for closing the tubes above has the disadvantage that after a few weeks the sulphuric acid begins to attack the cork. To overcome this defect, and at the same time facilitate the preparation and re-charging of the tubes, a form in which corks are entirely dispensed with was designed by Mr W. Blount, and is shown in fig. 20. The stoppers are of glass and are lubricated with vaseline. The air passes through them in the direction shown by the arrows. In

other respects the dimensions are the same as those of the tubes shown in fig. 19.

In physiological experiments it is often not necessary to measure exactly the air current passing through the absorption apparatus for moisture and

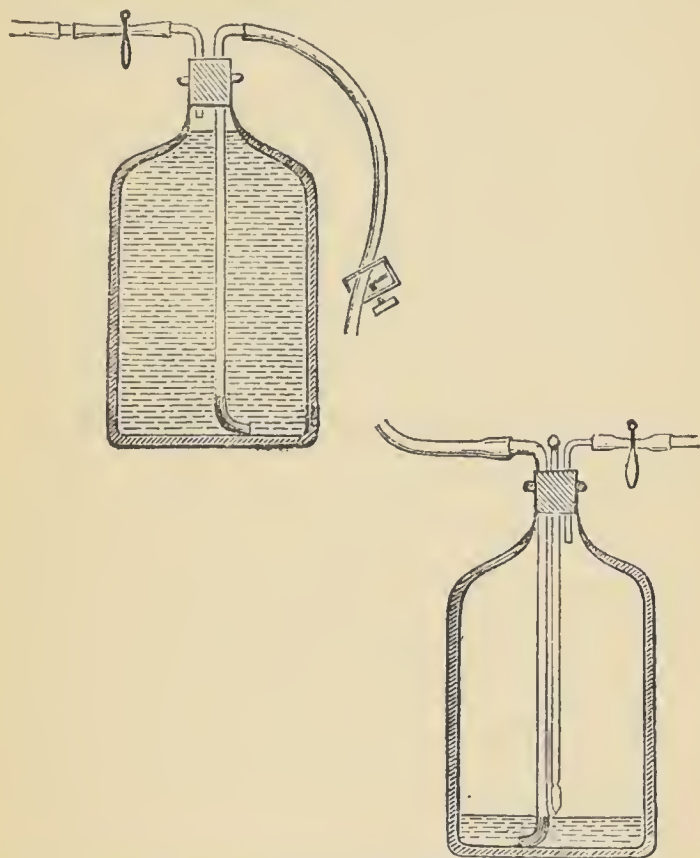


FIG. 21. — Aspirator for Determination of Moisture and Carbon Dioxide in Air.

carbon dioxide. When exact measurement is required this can be carried out by means of a wet gas-meter, or still more exactly by using an aspirator of known capacity. For many purposes the following form of aspirator is very convenient. Two bottles (fig. 21), each holding a little over 5 litres, or 10 litres, or any other

convenient amount, up to a mark in the neck, are arranged as shown in the figure, and connected together by a piece of stout, non-collapsible rubber tubing, provided with a screw clip for regulating the flow of water. The burette-clips are for starting or stopping the flow. The bottles are covered outside with a layer of felt, to keep the temperature of the air and water equal during an experiment, and also to prevent breakage. A vertical strip on each bottle is, however, left uncovered, so that the height of the water may be watched and the reading of the thermometer taken. The bottles are graduated roughly by fastening strips of paper at intervals of 1 litre up the uncovered strip of glass. It is thus easy to see that the water is running at about the proper rate.

To graduate the aspirator one of the bottles is allowed to drain for a minute, and is then weighed accurately. The two bottles are now connected, and the weighed bottle filled with water to the mark, the tubing also being filled with water. The rubber stopper of the weighed bottle is then removed, care being taken to let no water escape from the end of the long piece of glass tubing. The bottle filled with water is then weighed again; and by deducting from this weight that of the empty bottle, and making the usual small corrections, as in the graduation of a measuring flask, the volume of water held by the bottle filled to the mark, and with the tubing in position, is obtained. If a suitable balance is not available, this volume can be measured, though less accurately, with a large measuring cylinder. The

difference between the capacity of the bottle and some round volume, such as 5000 c.c., is now measured into the bottle, which has previously been emptied and drained for a minute. The stopper is then replaced, care being taken, as before, not to spill any of the water in the glass tubing. The other bottle is filled with water to the mark, and the aspirator is ready for use. It measures off exactly 5000 c.c., or whatever other volume has been chosen, each time the bottles are reversed and the lower one allowed to fill to the mark. The air measured is at the temperature shown by the thermometer, and is, of course, saturated with moisture.

In determining very exactly the percentage of carbon dioxide in outside air it may be desirable to use a very large aspirator. For this purpose a pair of large glass carboys, arranged on the same principle as that just described, are very convenient.

Determination of Carbon Dioxide.—The absorption apparatus (fig. 19) consists of a pair of test-tubes arranged in the same way as already described for absorption of moisture. The first tube is filled with soda-lime, and the second with sulphuric acid and pumice for absorbing the moisture given off by the soda-lime. The air must arrive perfectly dry at the absorption tube for carbon dioxide, and is therefore first passed through the absorption apparatus for moisture.

The soda-lime may be made by heating together in a copper vessel 1200 grammes of caustic soda in saturated solution and the product obtained by slaking to a fine powder 1000 grammes of quicklime. The

heating is continued until the soda-lime can be broken up in a mortar. The fragments are rapidly sifted through a wire sieve of about twelve meshes to the inch, and the product freed from powder by a finer sieve. Commercial soda lime similarly sifted may answer equally well, but is sometimes unsatisfactory. A piece of cotton-wool is placed between the cork and the soda-lime, as shown in the figure, in order to prevent any soda-lime from being carried over by a rapid air current.

The weight of carbon dioxide in the air aspirated through the apparatus is shown by the increase in weight of the pair of tubes. With good soda-lime, and only a small proportion of carbon dioxide in the air, the absorption is complete until about 500 litres of air have passed through, if the rate does not exceed about 1 litre per minute; but after this a second pair of tubes will usually begin to increase in weight. The absorption of carbon dioxide is thus not nearly so efficient as that of moisture, and unless the soda-lime is fresh it is well to use a second absorption apparatus for carbon dioxide in case of any appreciable failure of the first one.

The following is an example of results obtained when 90 litres of laboratory air, measured by a meter, were aspirated through two pairs of absorption tubes for carbon dioxide, at a rate of 1 litre per minute.

Increase of first pair	.	0.1615	gramme
„ second pair	.	0.0001	„

If the percentage of carbon dioxide in the air is required, the volume of air aspirated must be corrected

to dry air at 0° C. and 760 mm. barometric pressure. The number of c.c. of carbon dioxide in this air can then be calculated by dividing the number of milligrammes by 1.97, since 1 c.c. weighs 1.97 milligrammes.

The following instance of a determination of carbon dioxide in outside air will serve as an example. The volume of air aspirated was 30.0 litres, and the temperature in the aspirator was 11.0° C., while the barometric pressure was 753 mm. This volume of air, reduced to dry air at 0° C. and 760 mm., is 28.20 litres. The increase in weight of the absorption apparatus for carbon dioxide was 0.0162 gramme, corresponding to 0.00821 litre. The proportion by volume of carbon dioxide was therefore 0.0291 per cent. As, however, there might be an error in weighing of three decimilligrammes, the last decimal figure in the result has little significance.

DETERMINATION OF MOISTURE BY DRY- AND WET-BULB THERMOMETERS.

FOR most ordinary purposes the moisture in air can be determined with sufficient accuracy from the readings of dry- and wet-bulb thermometers. But apart altogether from the absolute amount of moisture in air, or the "relative humidity," the wet-bulb temperature is of great direct hygienic significance when it is much above 60° F. (15.5° C.). In warm mines, factories, etc., and in warm climates, the wet-bulb temperature is of great importance.

The dry- and wet-bulb temperatures of the air can be determined correctly out of doors (except on still days), or whenever there is a good air-current, from the readings of the ordinary fixed dry- and wet-bulb thermometers, if they are properly protected from the sun. Where, however, there is little or no air-current, as in a room indoors, or where the air is nearly still in a mine, a fixed dry- and wet-bulb thermometer does not give correct readings unless an artificial air-current is produced. An artificial current may be produced by means of a small fan driven by clockwork, as in the Assmann hygrometer. This is a somewhat cumbrous and expensive apparatus, however, and it is usually best to use two ordinary chemical thermometers and keep them

in brisk motion until the readings are obtained. It is now easy to obtain suitable thermometers at a very moderate price. They must read together, and correctly, at all parts of the scale, and the scales should be open and very plainly marked if they have to be read by artificial light. The bulbs should be long and narrow, to save waste of time in getting constant readings.

A layer of thin muslin is secured with thread round the bulb of one of them, and this is wetted with water, carried in a small bottle, just before use. The thermometers are held in one hand, with the bulbs well separated, and vigorously waved to and fro in the air to be tested, until the readings of both thermometers are perfectly steady. In reading the thermometers care must be taken that they are not affected by the heat of a candle or lamp. A pocket electric lamp is useful for making the readings. Unless the air is saturated with moisture the wet-bulb thermometer will read lower than the dry-bulb, and may often read considerably lower than a stationary wet-bulb thermometer.

To calculate from the readings the weight of moisture in a cubic foot of the air, the dew-point, the relative humidity (*i.e.* the percentage relation between the amount of moisture present and the amount which air saturated at the same temperature would contain), and the pressure due to the aqueous vapour present, Glaisher's well-known tables¹ should be used. The percentage by volume of the aqueous vapour present in the air is given

¹ *Hygrometrical Tables*, by James Glaisher, F.R.S. Published by Taylor and Francis, Red Lion Court, Fleet Street, London.

by reducing to a percentage the ratio of the pressure of aqueous vapour to the existing barometric pressure. Thus if the air is saturated at 64° F., the pressure of aqueous vapour is 0.596 inch of mercury. Hence if the barometric pressure is 30.0 inches the percentage of aqueous vapour by volume is $\frac{0.596}{30.0} \times 100 = 1.99$.

It is convenient to remember that between the temperatures of 40° and 70° F. the dew-point is approximately as many degrees below the wet-bulb reading as the wet-bulb reading is below the dry-bulb. The dew-point is the temperature at which, if the air were cooled, it would be just fully saturated with moisture, so that it could not be cooled further without depositing moisture. With the barometer at 30 inches the percentage by volume of the aqueous vapour in air fully saturated with moisture would be as shown in the following table. If the barometer were below or above 30 inches, the percentages would have to be proportionally increased or diminished.

Temperature, F.	Percentage of Aqueous Vapour by Volume.	Temperature, F.	Percentage of Aqueous Vapour by Volume.
12°	0.25	76°	3.0
27.5	0.5	81	3.5
45	1.0	85	4.0
56	1.5	88.5	4.5
64	2.0	92	5.0
70.5	2.5	95	5.5

Glaisher's tables give all the data in English measure (grains and cubic feet). One grain is 0.0648 gramme, one cubic foot 0.0283 cubic metre, and one inch 25.4 millimetres.

RECOGNITION AND DETERMINATION OF SMALL PROPORTIONS OF CARBON MONOXIDE IN AIR.

ON account of the poisonous properties of carbon monoxide, the frequency of its presence in air, and the impossibility of detecting small proportions of it by smell, tests by which it may be detected and estimated in air are of much practical importance. When present in considerable concentration it has a distinct garlic-like odour; but this is practically of no use in revealing its presence, as the odour is faint and is nearly always concealed by that of other gases or vapours present along with it. Most of the chemical reactions for estimating carbon monoxide are also more or less unreliable in ordinary cases, as they are given by other gases and vapours which may probably be present. Methods by which carbon monoxide may be determined when it is present by itself, or along with other combustible gases, have already been described above (pp. 28-39 and 53-58).

Testing with a Small Animal.—This method,¹ which was introduced by the writer as a means of testing for

¹ *Report on the Causes of Death in Colliery Explosions and Fires*, Parliamentary Paper [Cd. 8112], 1896; also Haldane and Douglas, *Trans. Inst. of Mining Engineers*, vol. xxxviii. p. 267, 1909.

dangerous proportions of carbon monoxide in the air of mines, depends upon the fact that while small warm-blooded animals are about as sensitive in the long run to carbon monoxide poisoning as large animals, including man, the small animals react far more quickly, and can therefore be used safely as indicators of the presence of carbon monoxide. A mouse, or a small bird, such as a canary or linnet, may be employed for the test. The bird is more sensitive to carbon monoxide; and it is easier to see whether a bird, sitting on its perch in a cage, is affected, as it becomes unsteady and falls off its perch. A bird is, however, very apt to die suddenly when in a dangerous atmosphere, and thus to become useless as a further guide. Roughly speaking, the bird or mouse is affected within about a tenth of the time required to affect a man. The actual time depends upon the percentage of carbon monoxide. If the bird or mouse is affected at all, it will show the effects within less than ten minutes. The bird will probably die (unless promptly removed) with anything more than about 0·2 per cent. of carbon monoxide in the air, while the mouse will probably be only disabled by this percentage, and may still live with 0·4 or 0·5 per cent. It seems probable that anything more than 0·2 per cent. would, after a sufficient time, be very dangerous to a man, while anything more than 0·02 per cent. might produce, after a sufficient time, headache and partial disablement.

A mouse does not show distinctly, by its symptoms, the presence of less than about 0·1 per cent. of carbon monoxide in the air; but its blood may be used to detect

as little as 0·01 per cent. The animal is left in the suspected air for 15 or 20 minutes, and then killed by drowning. If more than about 0·01 per cent. of carbon monoxide was present in the air, the blood, when sufficiently diluted and compared with fresh normal blood similarly diluted, will have a more or less pink tint; and from the degree of pinkness it is possible to estimate roughly the percentage of carbon monoxide which was present in the air.

The poisonous action of carbon monoxide is due to the fact that this gas combines with hæmoglobin, the coloured blood constituent which normally carries oxygen in loose combination from the lungs to the tissues. As the carbon monoxide takes the place of oxygen, the blood is more or less prevented from carrying oxygen, and the animal dies, if the process has gone far enough, from want of oxygen. The extent to which the hæmoglobin becomes saturated with carbon monoxide depends in the long run on the relative mass influences of the oxygen and carbon monoxide present in the blood as it leaves the lungs. In human blood at the body temperature the affinity of carbon monoxide for hæmoglobin is about 300 times greater than its affinity for oxygen. Hence in air (containing nearly 21 per cent. of oxygen) the hæmoglobin would finally become equally saturated with carbon monoxide and oxygen if 0·1 per cent. of carbon monoxide was present in the air and the blood were thoroughly saturated till no more gas was taken up or given off. With twice as much carbon monoxide in the air the hæmoglobin would be shared in the proportion

of 2 to carbon monoxide and 1 to oxygen, and so on (see fig. 23).

It can thus be readily understood that there will be a more or less definite relation between the proportion of carbon monoxide in the air and the extent to which the hæmoglobin has combined with carbon monoxide in the blood of an animal which has been sufficiently long exposed for maximum saturation of its blood with carbon monoxide to have been reached. Were this relation a constant one, we could infer the exact percentage of carbon monoxide in the air from a determination of the percentage saturation of the animal's hæmoglobin with carbon monoxide. In a living animal, however, the relation is disturbed by several factors, one being the fact that in an animal suffering from want of oxygen, owing to carbon monoxide poisoning, oxygen is actively taken up by the epithelial cells lining the lungs, and passed into the blood at a higher partial pressure than that of the air. In consequence of this the mass influence of the oxygen is increased, and carbon monoxide is correspondingly kept out. The extent to which this is the case varies a good deal in different animals; and consequently we can only form a rough idea, from examination of the blood, of the percentage of carbon monoxide in the air. Nevertheless, a rough estimate is often quite sufficient for practical purposes, so that the test by means of the blood of a mouse is often very useful.

To make the test, the skin of the drowned mouse should be slit up along the middle line of the abdomen and chest with a pair of scissors. The chest wall is then

removed after cutting through the ribs on each side, and the heart exposed. By holding the heart over the mouth of a test-tube two or three drops of blood are easily obtained. This blood should be diluted at once with a good deal of water, to prevent clotting. For the purpose of comparison a dilute solution of human blood, or any other normal blood, must now be prepared. The human blood solution can be prepared from a drop or two of blood squeezed out from a prick of the finger with a large-sized needle. This blood is diluted with water in a test-tube until its tint becomes yellow. Part of the solution is then taken in another test-tube, into which coal-gas is passed through a piece of rubber tubing. As the tubing is withdrawn, the mouth of the test-tube is closed with the thumb, and the blood solution shaken up vigorously for three or four seconds with the gas. It will now be found that the solution has become pink and contrasts strongly with the yellow solution in the first test-tube. The pink colour is not seen properly unless the blood is sufficiently diluted, but it is easy to judge of the proper dilution after one or two trials.

There are now three test-tubes containing blood solution: one being solution of normal blood, the second being the same solution saturated with carbon monoxide, and the third being the solution of blood from the mouse. The last will be stronger than the two former, and must be diluted with water until its colour is the same in *depth* as that of the other two. If carbon monoxide was present, the mouse blood solution will appear pinker than the normal blood. To make the

comparison, the two tubes are held up against the sky and changed from side to side in order to eliminate physiological errors in colour-perception. If the mouse blood is pinker, the degree to which it is saturated with

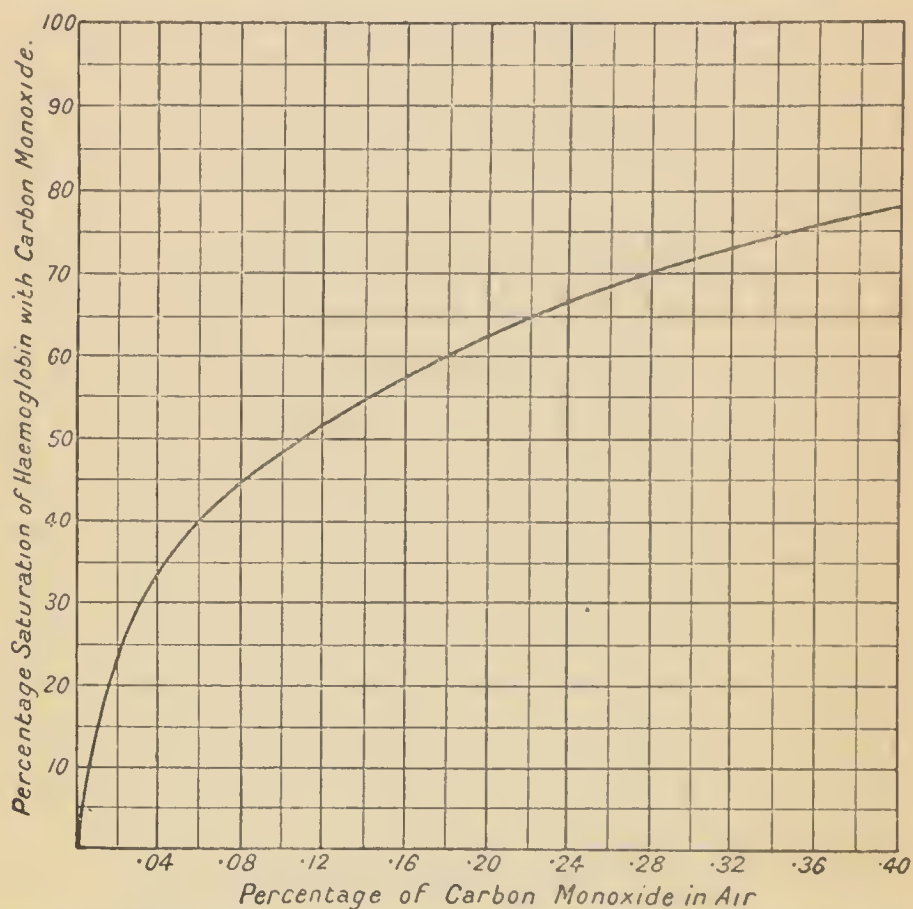


FIG. 22.—Curve showing Average Percentage Saturations of the Blood in Mice with Different Percentages of Carbon Monoxide in the Air.

carbon monoxide can be roughly estimated by comparing its degree of pinkness with that of the fully saturated blood. The estimate is, of course, only a very rough one.

The accompanying diagram (fig. 22) shows the average extent to which the blood of mice has been

found to become saturated with carbon monoxide in air containing different percentages of the gas. The data are taken from the results of experiments made for other purposes, but in which the composition of the air and percentage saturation of the blood were accurately determined. The difference in tint can be seen on careful examination when the blood is only 10 per cent. saturated, so that even with as little as .007 per cent. this test shows the presence of carbon monoxide.

The blood of a bird is not quite so delicate a test; and if a bird's blood is used, a drop of ammonia must be added to clear the solution.

Determination of Carbon Monoxide with Blood Solution.—Small percentages of carbon monoxide in air can be determined with considerable accuracy with the help of blood solution, the percentage saturation of the hæmoglobin with carbon monoxide being titrated by means of a solution of carmine. In many cases this is the only available method of determining small percentages of carbon monoxide in air; and in all cases it is a very useful and certain method, particularly as only a small sample of air is needed. The principle of the method is that a few c.c. of normal blood solution are shaken to saturation with the sample of air. A known volume of the normal blood solution is then taken, and standardised carmine added to it from a burette until (1) equality of pinkness with the solution saturated with the air sample is reached; and afterwards (2) until equality with the same blood solution fully saturated with carbon monoxide is reached. From the two results

the percentage saturation of the blood solution saturated with the sample of air can be deduced; and from this the percentage of carbon monoxide can be calculated.

The colorimetric titration is a peculiar one, since quality, and not depth of colour, is being estimated. The carmine has a bluer tint than blood solution saturated with carbon monoxide, and the mixture of the carmine colour with the yellow of normal blood solution reproduces accurately the tint of blood containing carbon monoxide. It must be remembered, however, that the equality of tint is physiological only, since the two solutions are not spectrally identical. The points of identity are not quite the same for different individuals, and are affected by the quality of the light. Nevertheless, the results of the analyses are the same for different individuals, although some persons, on account of defective colour-sense, may get less accurate results than others.

The sample of air is collected in the ordinary way, as described on p. 4, in a bottle holding about 100 c.c. or a little more. The use of vaseline for lubricating the stopper must be avoided, however, since the vaseline is apt to become suspended in the blood solution and render it turbid. The stopper should therefore be lubricated with glycerine. Sufficient ammoniacal blood solution (about 150 c.c.) is prepared to partly fill a small mortar, in which the bottle is inverted and the stopper removed under the blood solution. A curved glass tube of narrow bore is then introduced through the blood solution into the bottle, and sufficient air is allowed to

pass out to let about 5 c.c. of the blood solution pass up into the bottle. The stopper is then replaced securely and the bottle removed and wrapped up in a duster to shield it from light. It is then shaken as vigorously as possible for five minutes. It is hardly possible to continue the shaking for more than a minute at a time; but a rest can be taken for, say, fifteen seconds after each minute of shaking, in which case six minutes in all will be needed until the process is complete.

If the bottle is exposed to bright daylight during the shaking, the saturation will be far too low, and the method as originally described by the writer¹ was defective because no precautions were taken to exclude light. The previous addition of ammonia to the blood solution is also essential: otherwise the vigorous shaking will produce a precipitate, particularly if any carbon dioxide is present in the air. With gentle agitation, and no ammonia, the result is the same in the end; but the gentle agitation has to be continued for half an hour or more, and the insufficiency of the time allowed with gentle agitation was a further source of error in the method as formerly described.

The blood required for making the blood solution is easily obtained by pricking a finger with a large needle and squeezing out about 1 c.c. of blood. Unless the finger is warm the blood will not flow readily. By means of a narrow graduated pipette 0.75 c.c. of the blood (before it clots) is measured out into 150 c.c. of distilled water to which about 30 drops of strong

¹ *Journal of Physiology*, vol. xviii. p. 463, and vol. xxii. p. 478.

ammonia solution have been added. The solution is well mixed, and is now ready for use. It will be found that this strength of solution, when looked at in an ordinary test-tube, shows very satisfactorily the contrast in tint between normal blood and blood containing carbon monoxide.

For the titrations two test-tubes of equal bore (about .6 inch) are selected and marked as No. 1 and No. 2, the carmine being always added to No. 1 in the titrations. The carmine solution is prepared as follows. A comparatively strong stock carmine solution is first made by dissolving about half a gramme of carmine in strong ammonia and diluting to about 100 c.c. with distilled water. This solution should be preserved in a cool and dark place. The standard carmine solution is prepared fresh by adding a few drops of the stock solution to 100 c.c. of distilled water in a measuring cylinder of about the same diameter as the cylinder containing the blood solution; and sufficient of the stock carmine is added to make the depth of colour of the diluted carmine solution slightly greater than the depth of colour of the blood solution. A 20 c.c. burette is then filled with the diluted carmine, and another similar burette with distilled water.

The next step is to measure out 5 c.c. of blood solution into test-tube No. 1. with a pipette, and also pour about the same quantity into test-tube No. 2 and saturate it with coal-gas in the manner already described. Carmine is now added from the burette to test-tube No. 1 until its tint is about equal to that of No. 2. The depth of colour in No. 1 will, however, be too great, as the

carmine was purposely made of a rather deeper tint than the blood solution. Distilled water is therefore added till the depths are the same, and more carmine if necessary, until complete equality of tint and depth are attained. In making the comparisons the test-tubes should be held up against the sky, and it is absolutely essential to transpose them from one side to another at each observation. It will nearly always be found that the right-hand tube looks slightly pinker or yellower, or slightly deeper or less deep in tint, than the left-hand tube. This is in reality of great assistance in determining the exact point of equality.

When the point of equality is reached, the volumes of carmine solution and water added are read off on the two burettes. Distilled water is now added to the carmine in the cylinder in the same proportion as it had to be added to the carmine in test-tube No. 1. Let us suppose, for instance, that 6.0 c.c. of carmine and 1.2 c.c. of water had to be added to test-tube No. 1. The carmine in the cylinder would then have to be diluted in the proportion of 6.0 to $6.0 + 1.2$, or 5 to 6; and if 80 c.c. of carmine solution were left in the cylinder, 16 c.c. of water would have to be added. The carmine solution is now ready for use, and the burette is filled with it.

To determine the percentage saturation of the hæmoglobin in the solution which has been shaken in the bottle, this solution is poured out into test-tube No. 2 (after both test-tubes have been thoroughly washed out and as much adherent water as possible shaken out of them), and 5 c.c. measured from the pipette into No. 1.

Carmine is now added from the burette until the two tubes appear equal in tint. If the saturation is low, not more than 0.1 c.c. is added at a time when the point of equality is near, and in observing the tint the test-tubes are frequently transposed, the addition of carmine being continued until the tints again become unequal. It will probably be found that two readings of the burette give sensible equality of tint, and the mean of the two readings is taken as the correct one. If the saturation is over about 30 per cent., 0.2 c.c. is added at a time. The solution in No. 2 is now saturated with coal-gas, and a second determination made of the quantity of carmine required to produce equality. In this titration about 0.4 c.c. of carmine may be added at a time, since the higher the saturation the less effect has the carmine in altering the tint.

The following example will illustrate the method of calculating the result:—

Determination of First Point of Equality.

$$\begin{array}{rcl} 1.0 \text{ c.c. right} & \} & \\ 1.1 \text{ „ „} & \} & \text{Mean, 1.05.} \end{array}$$

Determination of Second Point of Equality.

$$\begin{array}{rcl} 6.8 \text{ c.c. right} & \} & \\ 7.2 \text{ „ „} & \} & \text{Mean, 7.0.} \end{array}$$

Thus, to produce the tint of complete saturation 7.0 c.c. of carmine had to be present in $7+5=12$ c.c. of the mixture; while to produce the tint of the solution from the bottle 1.05 c.c. of carmine had to be present in

$1.05 + 5 = 6.05$ c.c. of the mixture. The percentage saturation x is therefore given by the proportion sum :

$$\frac{7}{12} : \frac{1.05}{6.05} :: 100 : x.$$

Hence $x = 29.8$.

Test experiments with solutions made by diluting known mixtures of normal and fully saturated blood have shown that the results of the titrations can, with a little previous experience, be relied on to within 2 per cent. of the correct result. In the above example, for instance, the correct percentage saturation might be either 2 per cent. higher or lower.

It is unfortunate that neither the blood solution nor the carmine will keep. It is therefore necessary to prepare them fresh every day. The titrations must also be performed in daylight. In ordinary artificial light the difference in tint between the normal and the saturated blood solution is almost invisible. In working with blood solution the vessels used must be perfectly clean: otherwise the blood solution may begin to decompose within three or four hours, and will no longer give the full pink tint when it is saturated with carbon monoxide.

To calculate the percentage of carbon monoxide in the air from the percentage saturation of the blood solution with carbon monoxide, advantage is taken of the fact that the percentage saturation is proportional to the relative percentages of carbon monoxide and oxygen present, according to the law already explained. As the percentage of oxygen in ordinary air is practically

constant, the calculation becomes a very simple one, for the curve representing graphically the relation between percentage of carbon monoxide and percentage saturation is evidently a simple rectangular hyperbola; and

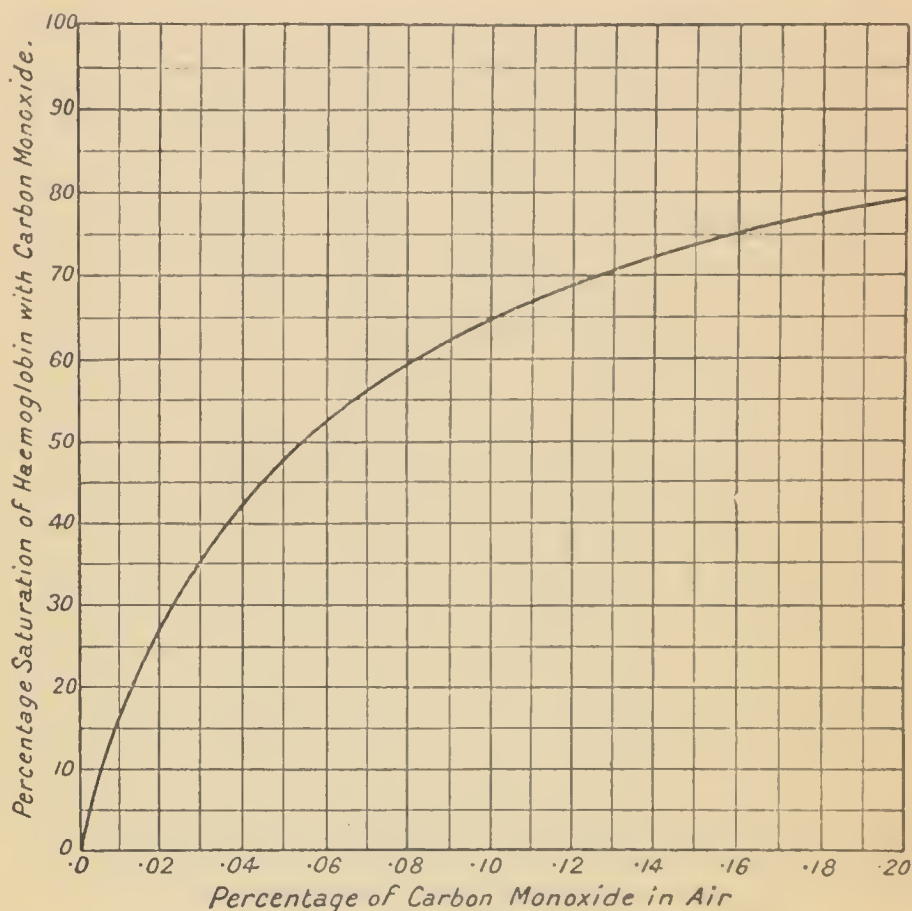


FIG. 23.—Curve showing Percentage Saturations of Human Blood Solution with Different Percentages of Carbon Monoxide in the Air.

the percentage of carbon monoxide in the air can be read off at once from this curve.¹ The actual curve for human blood solution at the ordinary room temperature of about 60° (15.5° C.) is shown in fig. 23. It will be

¹ If the percentage of oxygen in the air is considerably below normal, the percentage of carbon monoxide as read off from the curve must be

seen that the blood becomes half saturated in presence of 0·055 per cent. of carbon monoxide, a third saturated with 0·027 per cent., a fourth saturated with 0·014 per cent., etc. The percentage of carbon monoxide may also be calculated from the formula

$$P = \frac{S \times \cdot 055}{100 - S}.$$

P = percentage of carbon monoxide.

S = percentage saturation of the hæmoglobin.

The following are examples of determinations made with known mixtures of pure carbon monoxide and air.

Percentage Saturation of Hæmoglobin.	Percentage of Carbon Monoxide in Air	
	Calculated from Saturation.	Actually present.
50·3	·056	·052
48·0	·051	·052
30·0	·024	·026
19·8	·014	·013

This method of determination is only suitable for air containing less than about 0·2 per cent. of carbon monoxide. It may, however, be desirable to use it for higher percentages, in which case the sample must be diluted to a suitable extent with air. The bottle used for the saturation may be partly filled with water and inverted in a basin of water. A suitable volume of the correspondingly diminished. Thus, if there were only 10 per cent. of oxygen in the air in the bottle, the percentage of carbon monoxide would have to be multiplied by $\frac{1}{\frac{1}{21}}$. In other words, the test would be doubled in delicacy, though longer shaking would probably be needed.

sample is then measured off in a very small measuring cylinder and introduced under the water into the bottle, which is then allowed to fill up with air, transferred to a small basin of the blood solution, and the rest of the process carried out in the manner already described. To calculate the dilution, the capacity of the bottle must, of course, be known. The blood solution in the bottle will, of course, be diluted a little by water which adhered to the inside of the bottle; but this does not affect the titration. It is only necessary to tilt the test-tube No. 1 a little in order to make the depth of tint in the contained solution appear equal to that in No. 2 test-tube.

No other gas besides carbon monoxide gives the colour reaction with blood solution; and for detecting carbon monoxide this reaction is about five times as delicate as the older spectroscopic test.

RECOGNITION OF OTHER POISONOUS GASES.

THE recognition in air, or determination, by chemical tests, of commonly occurring poisonous gases and vapours other than carbon monoxide is usually of minor practical importance, as they may be recognised by smell or by their irritant action on the nose, eyes, and air-passages. This is the case, for instance, with chlorine, sulphurous acid, ammonia, acid fumes, sulphuretted hydrogen, phosphoretted hydrogen, nitrous fumes, and practically all the gases and vapours used in warfare. In any case, however, where the presence of a poisonous gas, for any reason difficult to detect, is suspected, the test with a mouse or bird may be employed. The smell of a poisonous gas is often difficult to detect on account of the presence of other odorous but possibly harmless substances.

Nitrous fumes, phosgene, and other lung-irritant gases or vapours used in warfare, are of special importance on account of their treacherous action. They have this in common, that a person exposed to them in sufficient concentration to produce comparatively slight irritation of the eyes and air-passages may die within the next day or two from acute inflammation of the lungs and air-passages. With other ordinary irritant gases there seems to be no such danger from a slight exposure, as any symptoms of irritation improve steadily after removal from the irritant atmosphere.

Nitrous fumes can be recognised chemically by the fact that a strip of paper moistened with a solution of starch

and a little iodide of potassium slightly acidified, is turned blue even when they are present in very great dilution.

Other gaseous impurities, such as sulphuretted hydrogen or hydrocyanic acid, are dangerous on account of their very rapid action, and in sewer air or smoke the smell of sulphuretted hydrogen is often masked.

The presence of sulphuretted hydrogen can easily be recognised chemically by the blackening of a strip of paper which has been dipped into acetate of lead solution. Any air in which this blackening occurs within a minute should be regarded as very dangerous. Sulphuretted hydrogen is about five times as poisonous as carbon monoxide, and much more rapid in causing death on the spot or dangerous after-effects.

Phosphoretted hydrogen, which is also extremely poisonous and treacherous in its action, may be recognised chemically by the fact that it blackens paper dipped in silver nitrate solution, but not paper dipped in lead acetate.¹

Arsenietted hydrogen, which is still more poisonous and treacherous, and acts cumulatively in very great dilution, can be detected readily by its action on a strip of filter paper which has been soaked in a solution of mercuric chloride and allowed to dry. The paper is turned yellow. Tests for a gas with a test paper are extremely rapid and delicate if the suspected air is allowed to blow on the paper.

¹ A method of determining phosphoretted hydrogen and arsenietted hydrogen is given by Dr Wilson Hake in the *Report to the Local Government Board by Dr Copeman, Dr Wilson Hake, and Mr Bennett, on Dangers arising from Ferro-Silicon*, Parliamentary Paper [Cd. 4958], 1909.

DETERMINATION OF DUST IN AIR.

IN view of the disastrous effects produced by the habitual inhalation of certain kinds of dust from hard stone, or of metallic dust, it is often important to determine the quantity of the dust, in order to judge of the efficacy of means taken to prevent its inhalation. The determination can be made as follows:—

A piece of glass tube about $2\frac{1}{2}$ inches long and $\frac{1}{2}$ inch in diameter is prepared in the form shown in fig. 24. A small plug of cotton-wool is pushed firmly down to the

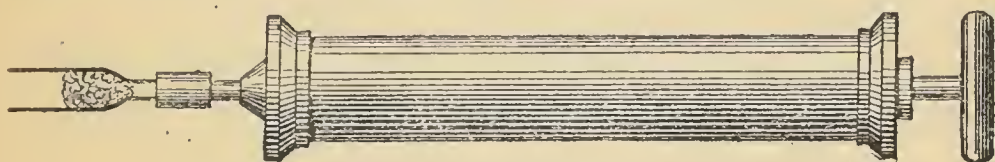


FIG. 24.—Apparatus for Dust Determination.

constricted part. This filters off any dust in the air drawn through the tube. An additional guard plug, or a cork at the wide end of the tube, serves to prevent accidental contamination, or loss of dust. At the place where it is desired to determine the dust (usually as near as possible to the place where it is given off into the surrounding air) the cork or guard plug is removed, and the glass tube attached by a piece of rubber tubing, about an inch long, to the nozzle of a brass exhausting

syringe taking about 200 c.c. or more of air at each stroke, and provided with thoroughly efficient valves. The glass tube should touch the nozzle of the syringe, so as not to require any support. The syringe is then held so that the tube points horizontally, and a sufficient quantity of air drawn through. The quantity is measured by counting the strokes of the syringe, the capacity of which has been measured beforehand by sucking air through a tube from a measuring cylinder inverted over water, or by attaching the syringe, with the tube and plug in position, to an experimental gas-meter. Care must be taken that at the end of each stroke time is given for the full charge of air to enter, as the resistance of the cotton-wool causes a slight delay.

After the air has been drawn through the tube the guard plug is replaced. If any dust was present in the air it will now be seen on the plug of cotton-wool. The further steps will depend on the nature of the dust and the object of the determination.

Stone Dust.—If the dust is from stone the plug of cotton-wool is ignited in a platinum crucible, carefully weighed to decimilligrammes, with the usual precautions as regards cooling. The difference in the weight of the crucible before and after ignition gives the weight of dust in the air. The weight of the ash from the cotton-wool is not appreciable. The quantity of air needed for the analysis depends, of course, on the amount of dust present. In the air of an “end” or “rise” in a mine, with a rock-drill boring dry holes, 10 litres of air would

usually be sufficient to give 50 to 100 decimilligrammes of dust. With an efficient jet of water to prevent dust no appreciable quantity of dust should be yielded by 20 litres of air.

Organic Dust.—The weight of the tube + cotton-wool is first ascertained after a few litres of air, dried by passing through a calcium chloride or sulphuric acid absorption tube, have been run through to dry the cotton-wool thoroughly. The same process is gone through after the dust has been collected, and the difference in weight gives the weight of dust in the air.

Lead Dust.—On account of the poisonous properties of lead it may be necessary to determine lead in the dust collected from the air of factories, etc., where lead is used. The following method, recommended by Vernon Harcourt,¹ may be employed:—Dilute nitric acid (10 per cent.) is poured, a few drops at a time, through the tube containing the plug into a beaker of about 50 c.c. capacity. The plug is then transferred to the beaker, the tube washed out, and the plug stirred and pressed with a glass tube sealed at the end, while the liquid is gently heated. Hydrofluoric acid, a few drops at a time, is then added directly (not down the glass) in order to dissolve lead silicate. The very dilute hydrofluoric acid has little action on the glass, but dissolves the particles of silicate suspended in the liquid. The liquid, amounting to about 20 c.c., is now passed through a small filter into a 50 c.c. measuring flask, and the beaker,

¹ *Report of the Departmental Committee on Lead Poisoning, etc.*, Parliamentary Paper [Cd. 5278], 1910, vol. ii. p. 120.

plug of cotton-wool, and filter washed with successive small portions of water till the flask is filled to the mark. After thorough mixing, a few c.c. of the liquid are then taken out in a pipette, and tested colorimetrically for lead after addition of sulphuretted hydrogen, etc., as described in a paper by Vernon Harcourt in the *Journal of the Chemical Society*, vol. xcvii. p. 841. If the colour is as pale as, or less pale than, that due to half a centimilligramme of lead, a larger proportion of the remaining liquid is used for a second testing, and the amount of lead calculated in the manner described in the paper.

Other metals, such as copper, etc., may be determined in the collected dust by similar methods when this is necessary.

Enumeration of Dust Particles by Kotzé Konimeter.

—In the case of the very dangerous dust produced by quartzite, flint, or other more or less pure siliceous stone, the pathological evidence shows that it is the very fine particles which are dangerous. It is hardly possible to estimate these fine particles gravimetrically, particularly as they are usually mixed with coarse particles which cannot be screened off. For these reasons another and far more convenient method has recently been introduced by Mr R. N. Kotzé, the South African Union Government Mining Engineer. By means of a piston worked by a spring and trigger, 5 c.c. of the air are projected through a fine nozzle against a glass slide smeared with vaseline. The dust particles in this air are caught on the vaseline, thus forming a circular "spot." With

the help of an arrangement in the eyepiece of a microscope the number of dust particles in two opposite sectors of this spot are counted with a $\frac{1}{2}$ -inch objective. These sectors form together a tenth of the spot, and thus contain the dust particles in 0.5 c.c. of air. A number of "spots" can be taken on the same slide, so that the air at different places can be sampled rapidly.

The method seems to be a very valuable one. A full description of it, with illustrative figures, has been given by Mr J. Innes in the *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, March 1918, p. 199.

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